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Multi-stimuli responsive amphiphilic diblock copolymers by a combination of ionic liquid-mediated cationic polymerization and recyclable alloy nanoparticle-mediated photoRDRP

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ABSTRACT

Poly(alkyl vinyl ether)-containing multifunctional block copolymers (BCPs) are challenging to synthesize and still limited in numbers despite their possible applications in high-tech areas. This article presents the synthesis of unprecedented amphiphilic poly(2-thioethyl vinyl ether)-*block*-poly(poly(ethylene glycol) methacrylate) (PTEVE-*b*-PPEGMA) BCPs via sequential ionic liquid-mediated cationic polymerization of CEVE and recyclable alloy-mediated photoRDRP of PEGMA, followed by post-polymerization modification of the pendant -CH_2CH_2Cl functionality to -CH_2CH_2SH. Controlled nature of both the cationic polymerization and photoRDRP was demonstrated by the first-order kinetic and linear increase of molecular weight with increase of monomer conversion, keeping low dispersity values. The synthesized PTEVE-*b*-PPEGMA BCP exhibited a dual (redox and temperature) stimuli-response. The cloud point of PTEVE-*b*-PPEGMA BCP can be tuned by changing the PEGMA mol% in the BCP. Amphiphilic PTEVE-*b*-PPEGMA diblock copolymer undergoes self-aggregation forming spherical nano-objects. These promising PTEVE-*b*-PPEGMA diblock copolymers could be used for many applications, including dual stimuli-responsive materials, materials with tunable hydrophobicity, and contaminant removal.

1. Introduction

Polyvinyl ethers (PVEs) have attracted significant interest due to their applications in gas-selective permeable membranes, transparent materials for optical lenses [1,2], bioinert interfaces [3,4], and hydrogen generation [5]. Block copolymers solely composed of vinyl ethers were prepared by living cationic polymerization technique [6], for application as polymer surfactants [7], stimuli-responsive gels [8,9], and thermoplastic elastomers [10]. However, for emerging applications of VE-containing polymers, synthesis of novel copolymers via covalent linking of two or more segments with diverse properties are required. Need for such novel copolymers with unique properties for the development of high-tech materials is continuously increasing. A wide range of reversible deactivation radical polymerization (RDRP) techniques have proliferated synthesis of well-defined copolymers composed of radically polymerizable monomers [11-14]. However, nonpolar olefins and VEs are not radically polymerizable [15,16], implying the requirement of multimode polymerization (combining two different types of polymerization such as cationic → RDRP and vice versa) for the synthesis of block copolymers containing such monomers [13].

Poly[poly(ethylene glycol) methacrylate] (PPEGMA) belongs to the poly(ethylene glycol)-functionalized (PEGylated) family of polymers which has received some attention both from academia and industry for their various applications in biomaterials, construction materials, tissue sealant development, protein stabilizers and drug delivery vehicles [17-19]. RDRP of PEGMA has been reported [20,21]. However, these RDRP processes suffer from the inadequate catalyst recovery process, which resulting toxicity and undesired color in the final product. Considering the wider potential application, the preparation of multifunctional copolymers based on 2-chloroethyl vinyl ether (CEVE, bearing a fragile C-Cl bond) and a functional PEGylated monomer (such as PEGMA) via the development of a facile transformation strategy from cationic polymerization to photoRDRP is a highly desirable objective.

Due to their unique properties, ionic liquids (ILs) have emerged as a green solvent for organic transformation/polymerization/ biochemical reactions [22-25]. ILs have been used as a solvent for cationic polymerization of isobutyl vinyl ether (IBVE) [26-28]. However, only Aoshima and coworkers were able to produce well-defined PIBVEs. In

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other two reports, PIBVEs with high dispersity (≥1.6) were produced. However, to the best of our knowledge, ambient temperature IL-mediated cationic polymerization of CEVE has not yet reported. Recently, IL-mediated sequential cationic polymerization was demonstrated to be quite efficient to prepare well-defined block copolymers with low dispersities ($Đ < 1.35$) [29]. In this context, the present article reports for the first time, how the combination of IL-mediated cationic polymerization of CEVE and alloy-mediated photoRDRP of PEGMA can be used to synthesize original PCEVE-*b*-PPEGMA BCPs and PTEVE-*b*-PPEGMA BCPs via post-polymerization modification of the pendant -CH_2CH_2Cl functionalities to -CH_2CH_2SH. The properties of the aqueous solutions of PTEVE-*b*-PPEGMA BCPs were examined in detail, specifically focusing on the micelle formation behavior and stimuli responsive behavior (temperature and redox responsivity). This approach may be useful for the preparation of well-defined polymers suitable for medical and engineering applications.

2. Experimental

1. *Materials*

All the chemicals were procured from Sigma Aldrich, unless stated otherwise. The monomers, 2-chloroethyl vinyl ether (CEVE, 99%) and poly(ethylene glycol)methacrylate (PEGMA, average M_n 360) were procured from Aldrich and were freed from inhibitors by passing them through a basic alumina column. PVPh-Ni_3Co_1 alloy nanoparticles [30] and 1-alkyl-3-methylimidazolium bromide ionic liquids (BMIMBr, HMIMBr, OMIMBr and DMIMBr) [31] were prepared by following earlier reported procedures.

2. *IL-mediated cationic polymerization of CEVE*

Typically, BMIMBr (86 mg, 0.392 mmol), $FeCl_3$ (159 mg, 0.98 mmol) and BEB (54 μL, 0.392 mmol) were taken in a round bottomed flask, degassed with N_2 bubbling and the flask was thermostated at 25 °C. Finally, degassed CEVE (1.0 mL, 9.8 mmol) was added to the mixture under magnetic stirring to start the reaction. During the polymerization, aliquots were withdrawn periodically to assess the monomer conversion (by gravimetry) and the molecular weights (M_ns) and dispersity values ($Đ$s) (by SEC). The polymerization was quenched with prechilled MeOH and the polymer was precipitated, dried and characterized by IR and NMR spectroscopy and SEC.

^1H NMR (400 MHz, DMSO-d_6, δ ppm of P15, Table S4 and Fig. 3): 1.05 (–$C\underline{H}_3$ of the α-chain end corresponding to the BEB initiator residue, signal e), 1.70 (–CH–$C\underline{H}_2$– of the CEVE repeat unit, signal a), 3.30 (–$OCH_2C\underline{H}_2Cl$ of the CEVE repeat unit, signal d), 3.65 (–C$\underline{H}$–CH_2– of the CEVE repeat unit, signal b and –$OC\underline{H}_2CH_2Cl$ of the CEVE repeat unit, signal c), 4.25 (a methine proton of the halide terminal, –$CH_2C\underline{H}(OCH_2CH_2Cl)$–Br of the ω-chain end of PCEVE, signal f).

2.3. *Synthesis of PCEVEs with varying M_ns*

PCEVEs of varying molecular weights (DP_n = 10–100) were prepared following the procedure described above, just by varying $[CEVE]_0/[BEB]_0$ ratios, keeping other reaction parameters constant, using the protocol described above.

2.4. *Synthesis of PCEVE-b-PPEGMA BCPs*

Syntheses of PCEVE-*b*-PPEGMA BCPs were carried out via alloy-mediated photoRDRP using PCEVE-Br (P15, Table S4) as the macroinitiator and PEGMA as the monomer under UVA (λ_{max} = 365 nm) irradiation, following a protocol developed by our group.[32]

^1H NMR (400 MHz, DMSO-d_6, δ ppm of P20, Table S5 and Fig. 3): 1.05–1.45 (–$C\underline{H}_3$ of the α-chain end corresponding to the BEB initiator residue, signal e and –$CH_2C(C\underline{H}_3)$ of the PEGMA repeat unit, signal b′), 1.45–1.95 (–CH–$C\underline{H}_2$– of the CEVE repeat unit, signal a and –$C\underline{H}_2C(CH_3)$ of the PEGMA repeat unit, signal a′), 3.30 (–$OCH_2C\underline{H}_2Cl$ of the CEVE repeat unit, signal d), 3.65–4.50 (–C$\underline{H}$ –CH_2– of the CEVE repeat unit, signal b, –$OC\underline{H}_2CH_2Cl$ of the CEVE repeat unit, signal c, –$OC\underline{H}_2CH_2$– of PEGMA repeat unit, signal c′ and –$OCH_2C\underline{H}_2$– of the PEGMA repeat unit, signal d′).

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5.Synthesis of thiol-functionalized PTEVE-b-PPEGMA via post-polymerization modification of PCEVE-b-PPEGMA

Pendant -CH_2CH_2Cl functionalities of PCEVE-*b*-PPEGMA BCP were transformed to -CH_2CH_2SH functionalities using NaSH/MeOH at room temperature by following a procedure reported by Chatterjee et al. [33]. Typically, $PCEVE_{25}$-*b*-$PPEGMA_{50}$ (P20, Table S5) was dissolved in anhyd. $CHCl_3$ under N_2 atmosphere and treated with NaSH/MeOH. After the reaction, the polymer was collected by centrifugation and dried to obtain the product.

^1H NMR (400 MHz, DMSO-d_6, δ ppm, Fig. 3): 0.65 (–$OCH_2CH_2S\underline{H}$ of the CEVE repeat unit, signal f), 1.05–1.45 (–$C\underline{H}_3$ of the α-chain end corresponding to the BEB initiator residue, signal e and –$CH_2C(C\underline{H}_3)$ of the PEGMA repeat unit, signal b′), 1.45–1.95 (–CH–$C\underline{H}_2$– of the CEVE repeat unit, signal a and –$C\underline{H}_2C(CH_3)$ of the PEGMA repeat unit, signal a′), 3.30 (–$OCH_2C\underline{H}_2Cl$ of the CEVE repeat unit, signal d), 3.65–4.50 (–C$\underline{H}$–CH_2– of the CEVE repeat unit, signal b, –$OC\underline{H}_2CH_2Cl$ of the CEVE repeat unit, signal c, –$OC\underline{H}_2CH_2$– of PEGMA repeat unit, signal c′ and –$OCH_2C\underline{H}_2$– of the PEGMA repeat unit, signal d′).

6. *Preparation of the S-S crosslinked copolymer network*

S-S crosslinked copolymer network was prepared following a procedure reported by Rosenthal et al. [34]. Typically, $PTEVE_{25}$-*b*-$PPEGMA_{50}$ BCP was treated with Et_3N (1:1.25 equivalent ratio) under N_2 atmosphere and cooled to 0 °C. Then H_2O_2 (2 equivalent, 3% aqueous solution by weight) was added to the flask and the mixture was purged with air for 2 h at 55 °C to allow the aerial oxidation of -SH to S-S. After the reaction, the product was collected by precipitation.

7.Reduction-triggered degradation of the S-S crosslinked copolymer network

Typically, 6 mg of the S-S crosslinked copolymer was dispersed into 2 mL DI water and treated with dithiothreitol (0.8 mL, 50.05 mM) at 25 °C. The degradation of the crosslinked copolymer networks to-SH was monitored by the turbidity change with time by UV–visible spectroscopy.

8. *Aggregation procedure*

1 mg of the PTEVE-*b*-PPEGMA BCP was dissolved in water and kept in a closed vial for a predetermined time.

9. *Dye uptake procedure*

Typically, 3 mg of PTEVE-*b*-PPEGMA BCP was added to the dye solution (3 mL) and allowed to stand undisturbed for 12 h. The amount of dye uptake was monitored by UV–Vis Spectroscopy via changes in the absorbance of the dye. Finally, the dye incorporated polymer nanospheres were isolated by centrifugation and washed to get rid of any surface adsorbed dye. Finally, the dye-loaded polymer nanosphere dispersion was analyzed by fluorescence spectroscopy and fluorescence microscopy technique. %Encapsulation was calculated using the following equation:

$$\%Encapsulation = \frac{Absorbance_{t=0} - Absorbance_{t=t}}{Absorbance_{t=0}} \times 100$$

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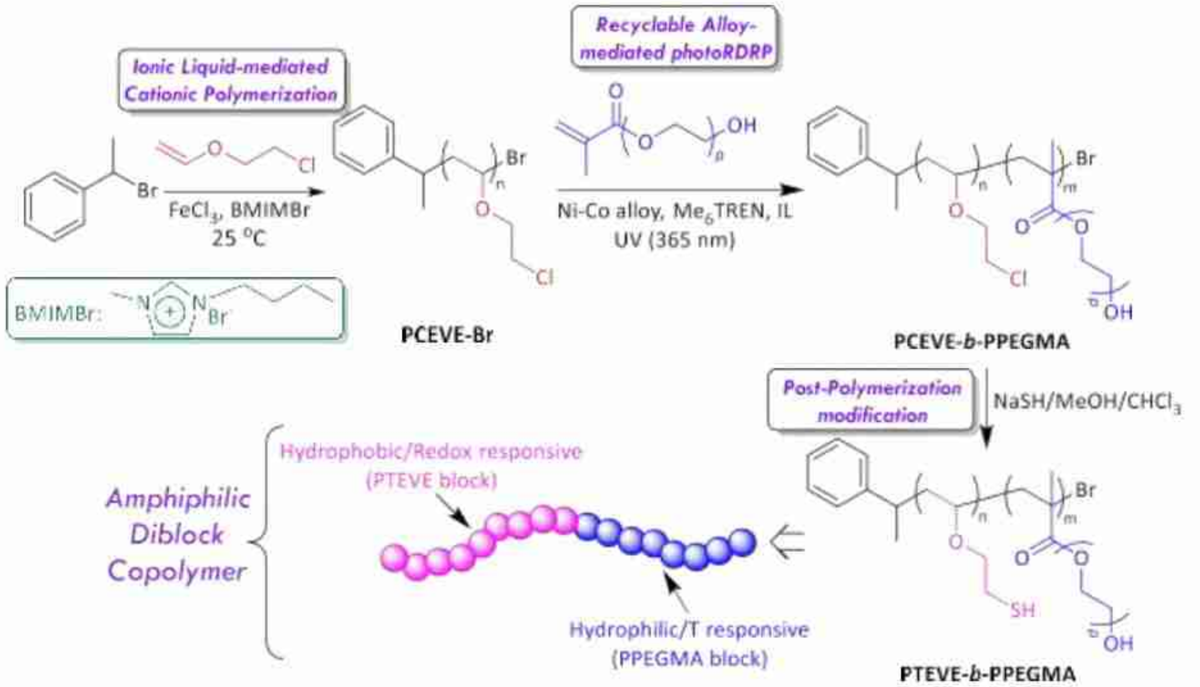

Scheme 1. Synthesis of amphiphilic PTEVE-*b*-PPEGMA diblock copolymers by a combination of cationic polymerization, photoRDRP and post-polymerization modification.

2.10. Characterization

The chemical structure of the products was determined by NMR (Bruker 400 MHz spectrometer) at 25 °C. IR spectra are recorded on a Perkin Elmer Spectrum 100 with a diamond crystal, using 16 scans per spectrum and a resolution of 4 cm^{-1}. Molar masses (M_ns) and dispersities ($Đ$s) were determined by a size exclusion chromatography (SEC) (from Agilent Technologies) in DMF (containing 0.1 wt% of LiCl) as the eluent. Temperature responsiveness of the PTEVE-*b*-PPEGMA diblock copolymer solution was measured on a Shimadzu UV-2600 spectrophotometer equipped with a temperature-controlled sample holder. The transmittance of the polymer solution was monitored in the temperature range of 10 to 80 °C at a detection wavelength of 500 nm, at a heating rate of 1 °C min^{-1}. FESEM analysis was performed using Zeiss Gemini SEM500 at an accelerating voltage of 5 kV. Photoluminescence (PL) spectra of the samples were recorded in a Fluorolog FL3-211 (HORIBA Scientific) with a 450-Watt Xenon arc lamp. Fluorescence microscopy images were recorded using a light microscope (DM2700M, Leica).

3. Results and discussion

1. IL-mediated cationic polymerization of CEVE

Four different imidazolium-based ILs (BMIMBr, HMIMBr, OMIMBr and DMIMBr) were tested in the IL-mediated controlled cationic polymerization of CEVE catalyzed by FeCl$_3$ using BEB as the initiator at 25 °C (Scheme 1). Results of the initial trials (P1-P4, Table S1, see Supplementary Material) established BMIMBr as the most suitable IL to ensure ultrafast polymerization, yielding well-defined PCEVE (P1, Table S1). Blank experiments (P5-P7, Table S2, see Supplementary Material) performed in the absence of BMIMBr, but in the presence of an organic solvent (such as DCM or toluene) establish that BMIMBr is indeed required to achieve ultrafast controlled polymerization of CEVE.

In order to identify the optimum BMIMBr concentration required to achieve controlled polymerization, a series of polymerization reactions were carried out using different concentrations of BMIMBr ([CEVE]$_0$/[BMIMBr]$_0$ ratio ranging from 1.25 to 25.0), keeping other reaction parameters same. Results of these reactions suggested that the

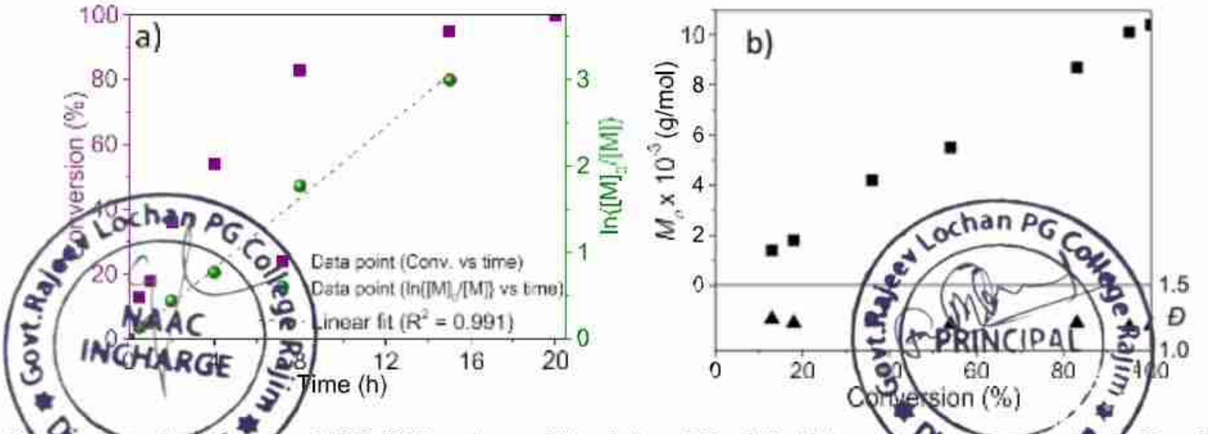

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Fig. 1. Plot of a) Conversion (%) vs. time, ln([M]$_0$/[M]) vs. time, and b) evolution of M_n and $Đ$ with increasing monomer conversion for IL-mediated cationic polymerization of CEVE; [CEVE]$_0$/[BMIMBr]$_0$ = 5.

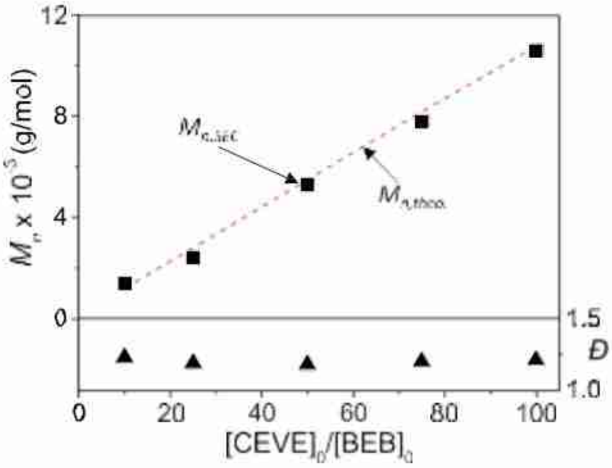

Fig. 2. Plot of M_n and $Đ$ vs. [CEVE]$_0$/[BEB]$_0$ for IL-mediated cationic polymerization of CEVE at 25 °C using BEB as the initiator (P14-P18, Table S4).

polymerization was ultrafast (completed instantaneously) at [CEVE]$_0$/[BMIMBr]$_0$ = 25 (P8, Table S3). The rate of polymerization was found to be decreased with increasing BMIMBr concentration [CEVE]$_0$/[BMIMBr]$_0$ = 10 to 1.67 (P9—P12, Table S3). The polymerization was extremely sluggish at a high concentration of BMIMBr ([CEVE]$_0$/[BMIMBr]$_0$ = 1.25, P13, Tabl S3), producing only trace amount of polymer. These experiments establishes [CEVE]$_0$/[BMIMBr]$_0$ = 25 as the optimum BMIMBr concentration to achieve ultrafast polymerization, yielding well-defined PCEVE.

Due to the fact that polymerization using [CEVE]$_0$/[BMIMBr]$_0$ = 25 finished instantaneously, we could not study the polymerization kinetics. Instead, detailed kinetic study was performed at [CEVE]$_0$/[BMIMBr]$_0$ = 5 which allowed somewhat slower polymerization (please compare P8 with P10 in Table S3, see Supplementary Material). Results revealed that the IL-mediated cationic polymerization of CEVE exhibited all the features of a controlled polymerization such as first order kinetics and linear increase of M_n with conversion, with low $Đ$s (1.18–1.23) (Fig. 1).

Successful synthesis of well-defined PCEVEs of varying M_n (from 1500 up to 10400 g mol^{-1}, maintaining low $Đ$s, simply by varying the initial [CEVE]$_0$/[BEB]$_0$ feed ratio from 10 to 100 (Fig. 2 and Table S4, see Supplementary Material) further established the controlled nature of the polymerization.

Structural characterization of PCEVE, synthesized via IL-mediated polymerization was performed using NMR (Fig. 3) and IR (Fig. S2, see Supplementary Material) spectroscopy. ^{1}H NMR spectrum of the synthesized PCEVE displayed the characteristic signals at 1.05 (–C$\underline{H}_3$ of the α-chain end corresponding to the BEB initiator residue, signal e), 1.70 (–CH–CH$_2$– of the CEVE repeat unit, signal a), 3.30 (–OCH$_2$C$\underline{H}_2$Cl of the CEVE repeat unit, signal d), 3.65 (–CH–CH$_2$– of the CEVE repeat unit, signal b and –OC$\underline{H}_2$CH$_2$Cl of the CEVE repeat unit, signal c), 4.25 (a

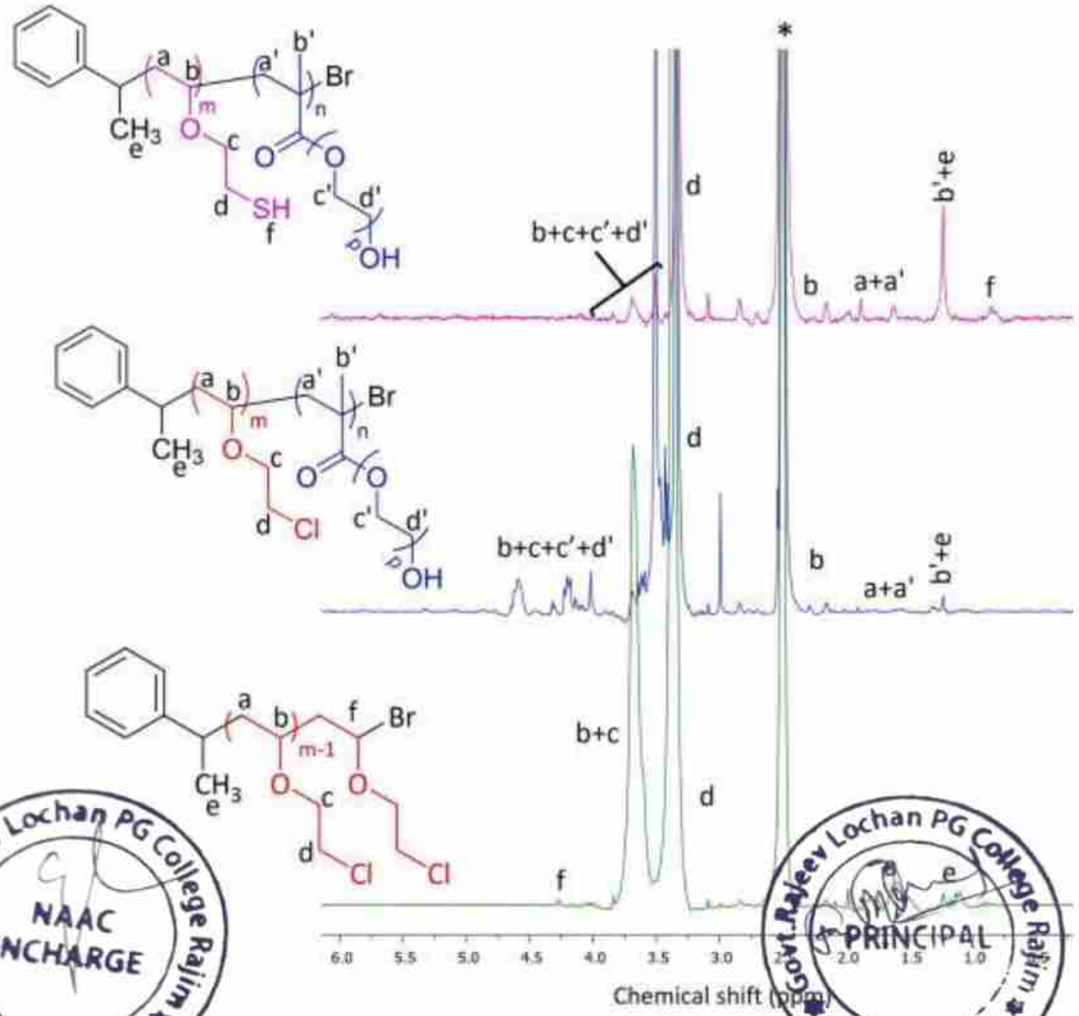

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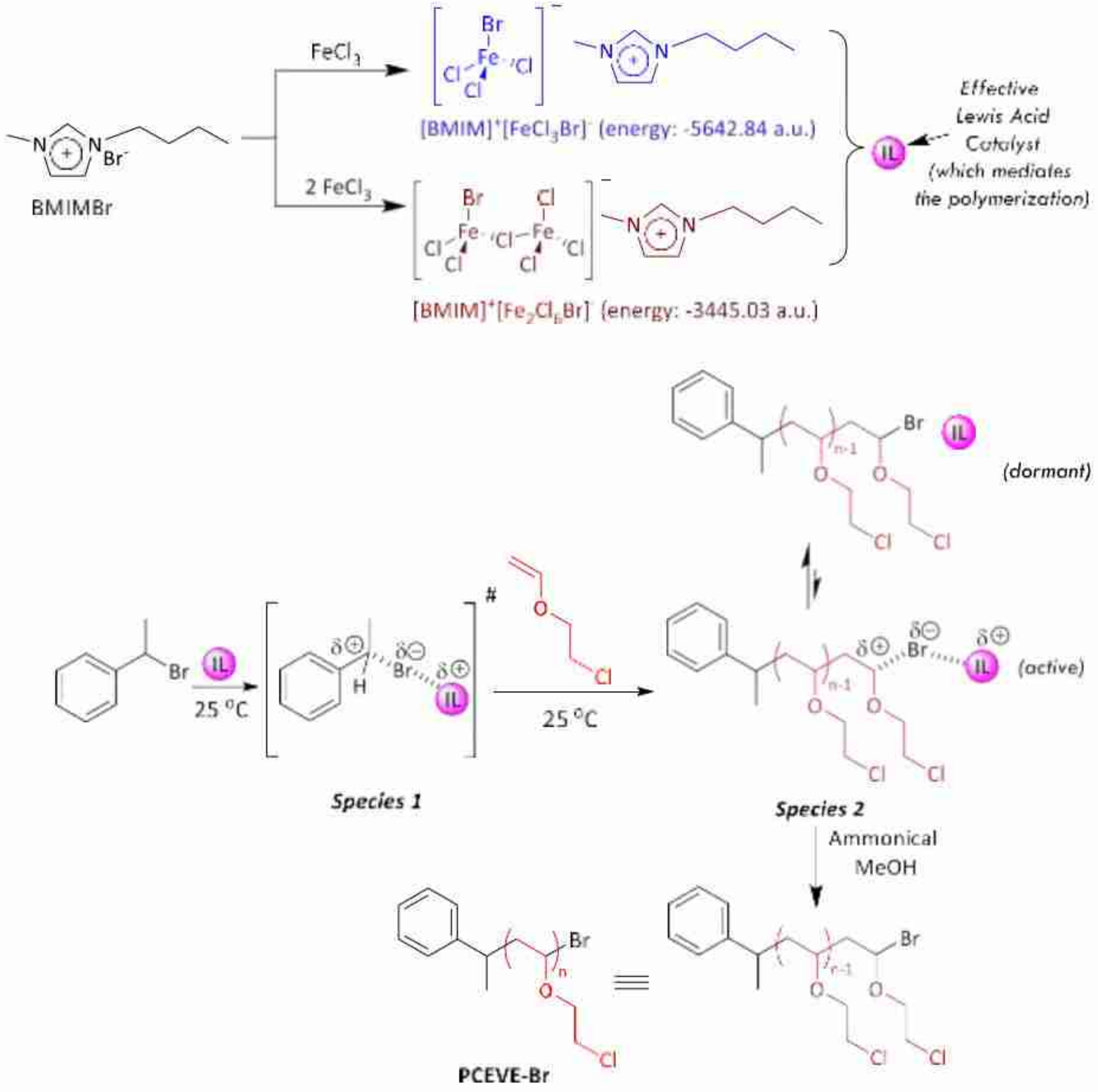
Fig. 3. ^{1}H NMR spectra of PCEVE$_m$-Br (in DMSO-d_6, P15, Table S4), PCEVE$_m$-b-PPEGMA$_n$ (in DMSO-d_6, P20, Table S5) and PTEVE$_m$-b-PPEGMA$_n$ (in DMSO-d_6, obtained after post-polymerization modification of P20, Table S5). * represents DMSO-d_6 resonance.



Scheme 2. Plausible mechanism of ionic liquid-mediated cationic polymerization of CEVE.

methine proton of the halide terminal, $-CH_2CH(OCH_2CH_2Cl)-Br$ of the ω-chain end of PCEVE, signal f).[35-37] ATR-IR spectrum of a representative PCEVE sample (Fig. S2) clearly showed the main characteristic peaks at 662, 742, 1107 and 2870–2960 cm^{-1}, attributed to -C-Cl (stretch.), C-O-C (stretch.), and -C-H (sym. stretch. and asym. stretch.) respectively.[38,39]

Based on the above results of the IL-mediated cationic polymerization of CEVE and successful reactivation of the PCEVE-Br chain ends in situ chain extension reaction (Fig. S1, see Supplementary Material), a plausible mechanism for the polymerization is proposed (Scheme 2). This mechanism is based on the detailed mechanistic study of IL-mediated cationic polymerization of St, recently reported by our group (please refer to Scheme 2 and the associated text of that paper).[29] This in situ generated effective Lewis Acid catalyst $[IL]^+[Lewis\ Acid]^-$[26,40,41] produces cationic species, $Ph-CH(CH_3)^{\delta+}-Br^{\delta-}-IL^{\delta+}$ via abstraction of the Br from BEB. Subsequently, addition of CEVE monomers to the active cation produces well-defined polymer, induced by $[BMIM]^+[FeCl_3Br]^-$ and $[BMIM]^+[Fe_2Cl_6Br]^-$.

3.2. Syntheses of PCEVE-b-PPEGMA diblock copolymers

A range of PCEVE-*b*-PPEGMA block copolymers (BCPs) were synthesized (Scheme 1) via recyclable alloy-mediated photoRDRP of PEGMA upon irradiation with UVA (λ_{max} = 365 nm) using PCEVE-Br macroinitiator (obtained by the IL-mediated controlled cationic polymerization of CEVE) (Table S5, see Supplementary Material). Narrow unimodal SEC traces of the BCPs (Fig. 4) demonstrating clear shifts towards higher molar masses, showing little/no remaining PCEVE-Br macroinitiator, indicates effective preparation of the BCPs. Alloy-mediated photoRDRP of PEGMA from PCEVE-Br macroinitiator exhibited typical features of RDRP process such as linear dependency of $\ln\{[M]_0/[M]\}$ vs. time (Fig. S3a) and a linear growth of M_n with conversion (retaining low $Đ$ values) (Fig. S3b).

The structure of the PCEVE-*b*-PPEGMA block copolymers was analyzed by ^1H NMR and IR spectroscopy. ^1H NMR spectrum (Fig. 3) of the $PCEVE_{25}$-*b*-$PPEGMA_{50}$ BCP (P20, Table S5, see Supplementary Material) exhibits the characteristic features of both the PCEVE[35-37] and PPEGMA[32,42] blocks at 1.05–1.45 ($-C\underline{H}_3$ of the α-chain end corresponding to the BEB initiator residue, signal a and $-CH_2C(C\underline{H}_3)$ of the PEGMA repeat unit, signal b), 1.45–2.05 ($-CH-C\underline{H}_2-$ of the CEVE repeat

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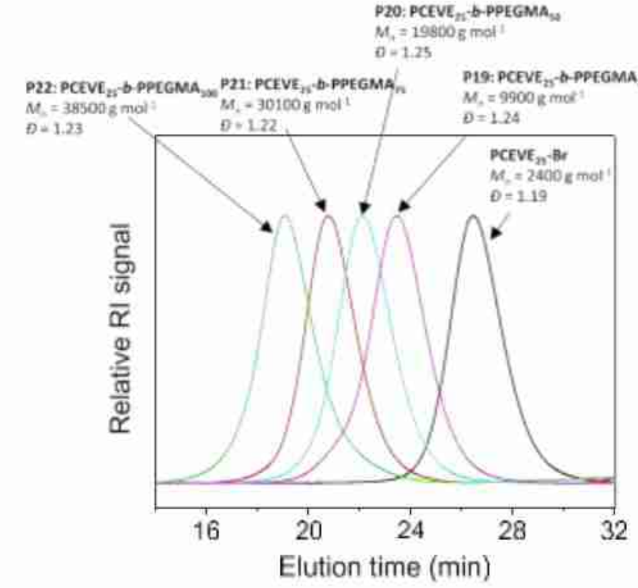

Fig. 4. SEC traces of PCEVE$_{25}$-Br (P15, Table S4) and, PCEVE$_{25}$-*b*-PPEGMA $_n$ (where n = 25, 50, 75, 100, P19-P22, Table S5) block copolymers.

unit, signal a and $-C\underline{H}_2C(CH_3)$ of the PEGMA repeat unit, signal a′), 3.30 ($-OCH_2C\underline{H}_2Cl$ of the CEVE repeat unit, signal d), 3.65–4.50 ($-C\underline{H}-CH_2-$ of the CEVE repeat unit, signal b, $-OC\underline{H}_2CH_2Cl$ of the CEVE repeat unit, signal c, $-OC\underline{H}_2CH_2-$ of PEGMA repeat unit, signal c′ and $-OCH_2C\underline{H}_2-$ of the PEGMA repeat unit, signal d′). IR spectrum of PCEVE-*b*-PPEGMA (Fig. S2, see Supplementary Material) exhibited characteristic absorption band corresponding to PCEVE segment [662, 742, 1107 and 2870–2960 cm^{-1}, attributed to –C–Cl (stretch.), C–O–C (stretch.), and –C–H (symmetric stretch. and asymmetric stretch.) respectively] [38,39] and PPEGMA segment [861, 947, 1096, 1259, 1452, 1725, 2870–2960 and 3453 cm^{-1}, attributed to $-CH_2-O$ (stretch.), C–O–C (stretch.), $-CH_2$ (sym. stretch.), $-CH_2$ (asym. stretch.), C=O (stretch.), –C–H (sym. stretch. and asym. stretch.) and –OH stretch, respectively] [43].

3.3. Synthesis of -CH_2SH functionalized PTEVE-b-PPEGMA diblock copolymers

Post-polymerization modification of the pendant $-CH_2CH_2Cl$ functionalities of PCEVE-*b*-PPEGMA diblock copolymers to $-CH_2CH_2SH$ functionalities was carried out using NaSH/MeOH. The successful transformation of $-CH_2CH_2Cl$ functionalities to $-CH_2CH_2SH$ functionalities was confirmed by the disappearance of the –C–Cl stretching bands at 662 cm^{-1} and the appearance of C-S stretching bands at 801 cm^{-1} (Fig. S2).[44] ^{1}H NMR spectrum of the PTEVE-*b*-PPEGMA copolymer (Fig. 3) reveals appearance of a new peak of -SH protons[33] in addition to all the characteristic peaks of both the blocks.[32,35-37,42].

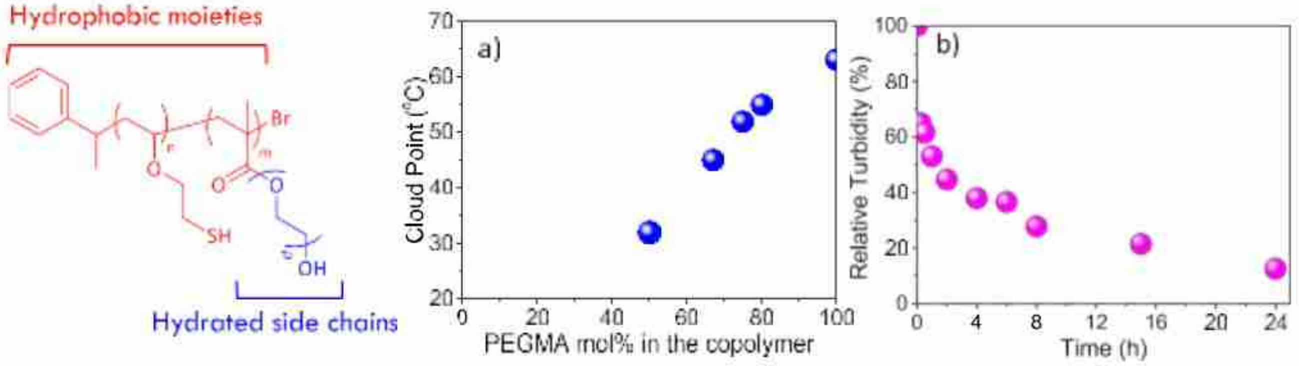

Fig. 5. (a) Evolution of T_{CP} vs. PEGMA content in PTEVE-*b*-PPEGMA BCPs. (b) Investigation of the redox induced degradation of the crosslinked copolymer network by turbidity measurements.

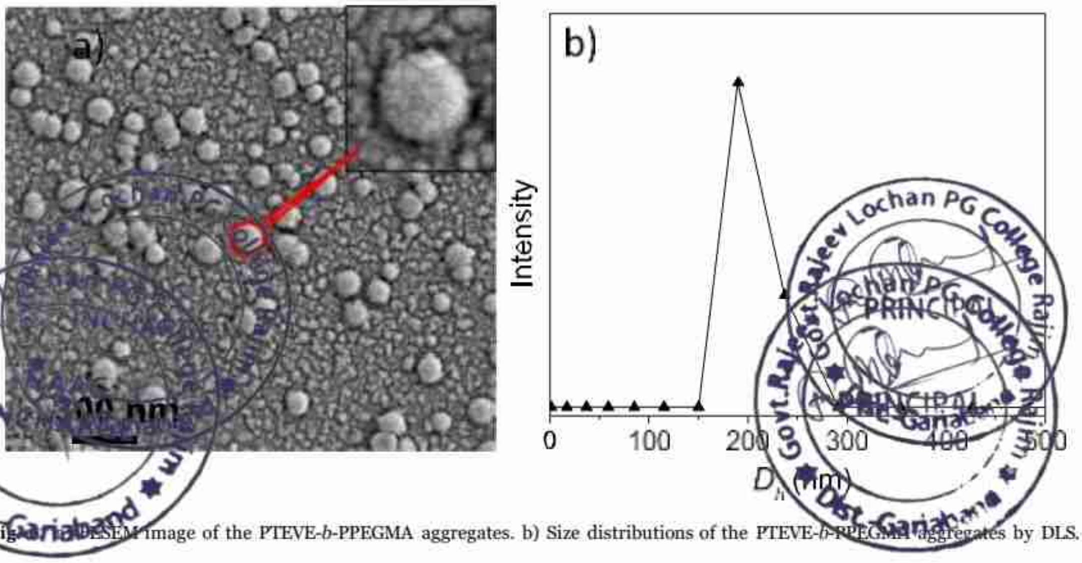

Fig. 6. a) FESEM image of the PTEVE-*b*-PPEGMA aggregates. b) Size distributions of the PTEVE-*b*-PPEGMA aggregates by DLS.

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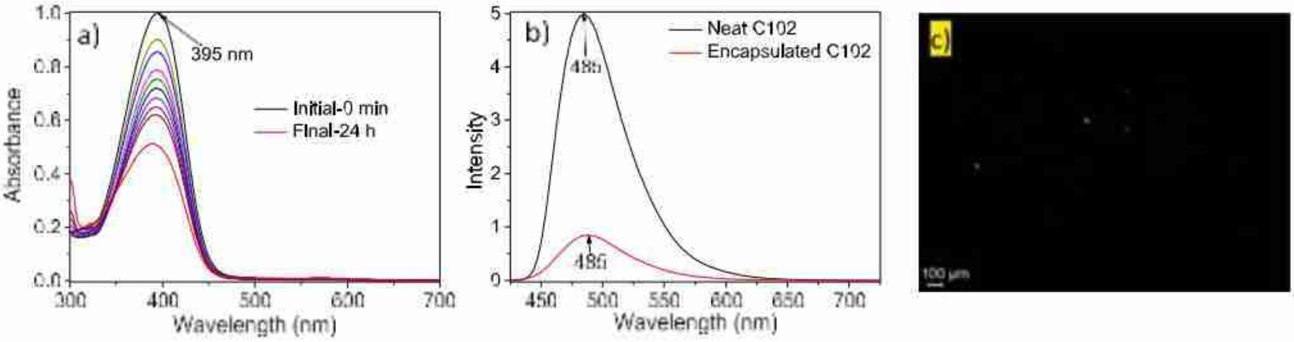

Fig. 7. (a) Time dependent UV–Vis spectra, (b) fluorescence emission spectra and (c) fluorescent light microscopy image during dye encapsulation experiment of PTEVE$_{25}$-*b*-PPEGMA$_{50}$ copolymer.

4.Temperature and redox response of PTEVE-b-PPEGMA diblock copolymers

-CH$_2$CH$_2$SH functionalized PTEVE-*b*-PPEGMA BCPs were expected to display redox and temperature responsiveness because of the properties of PTEVE (bearing -SH functionalities)[45-47] and PPEGMA[48] segments, respectively. Cloud point (T_{CP}) of PPEGMA homopolymer was estimated to be 63 °C,[49] whereas that of PTEVE-*b*-PPEGMA BCPs can be tuned simply by varying the hydrophobic PTEVE content in the copolymer. Increasing hydrophobic PTEVE content in the copolymer led to lowering of T_{CP}. Notably, T_{CP} of PTEVE$_{25}$-*b*-PPEGMA$_{25}$ copolymer with 50% PTEVE content was estimated to be 32 °C (Table S5 and Fig. 5a).

In order to investigate the redox responsive behavior of the PTEVE-*b*-PPEGMA BCPs, first S-S crosslinked polymer network was prepared (see Experimental Section). Upon subsequent addition of DTT, disulfide (S-S) bonds were reduced to thiol groups, leading to cleavage of the crosslinked polymer network, lowering of solution turbidity and concurrent growth of the intensity for transmission light with time, as revealed by UV–Vis spectroscopic analysis (Fig. 5b). It is to be noted that the solution turbidity levels off to ~13% of the initial value, instead of reaching to near zero. This is attributed to the fact that the formed oligomers could also absorb light, leading to a decrease of the transmittance light intensity, as reported earlier [50,51].

5. Self-aggregation behavior of PTEVE-b-PPEGMA diblock copolymers

The amphiphilic PTEVE$_{25}$-*b*-PPEGMA$_{50}$ BCP is comprised of hydrophobic PTEVE and hydrophilic PPEGMA segments. Self-aggregation of the PTEVE-*b*-PPEGMA copolymers in water was investigated to assess their amphiphilicity. Self-aggregation of PTEVE-*b*-PPEGMA copolymers led to nanospherical aggregate formation, as revealed by FESEM (Fig. 6a, D_{FESEM} = 133 ± 28 nm) and DLS analysis (Fig. 6b, D_h = 220 ± 70 nm).

In order to investigate the aggregation process further, incorporation of a hydrophobic dye, coumarin 102 (C102,) into the hydrophobic core of the aggregated nanospheres during the aggregation of PTEVE$_{25}$-*b*-PPEGMA$_{50}$ copolymer was investigated. Results revealed that C102 absorbance (at 395 nm) decreased steadily with time leading to ~49% encapsulation of C102 after 24 h (Fig. 7a). This result is comparable to the dye encapsulation efficiency of the reported amphiphilic copolymers, including amphiphilic copolymers based on dendritic polyethylene grafted by polyhydroxyethylmethacrylate and polyhydroxypropylmethacrylate [52], poly(β-amino ester)-*graft*-poly (ethylene glycol) copolymers [53] and poly(glycidyl methacrylate)-*block*-poly(n-butyl methacrylate) [54]. The fluorescence emission spectrum of PTEVE$_{25}$-*b*-PPEGMA$_{50}$ copolymer (Fig. 7b) with encapsulated C102 exhibited a similar peak, albeit of reduced intensity compared to the solution containing neat C102. This suggested encapsulation of C102 during self-aggregation of PTEVE$_{25}$-*b*-PPEGMA$_{50}$ copolymer. Fluorescence light microscopic image (Fig. 7c) depicts green light-radiating beads of C102-encapsulated spheres of PTEVE$_{25}$-*b*-PPEGMA$_{50}$ copolymer, confirming successful dye encapsulation.

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4. Conclusion

Herein, we report, the development of a facile approach towards the synthesis of well-defined multi-stimuli responsive amphiphilic PTEVE-*b*-PPEGMA BCPs via a combination of ionic liquid-mediated cationic polymerization of CEVE and alloy-mediated recyclable photoRDRP of PEGMA using PCEVE-Br macroinitiator (without any transformation of the initiating sites), followed by post-polymerization modification of the pendant -CH$_2$CH$_2$Cl functionalities to -CH$_2$CH$_2$SH functionalities. Detailed kinetics study of both the cationic polymerization and photoRDRP established controlled polymerization in both the cases. PTEVE-*b*-PPEGMA BCPs exhibited dual (redox/temperature) stimuli responsive behavior and tunable cloud point upon changing PEGMA content in the BCP. Use of "green" ionic liquid and recyclable catalyst make this process suitable for wider applications in the synthesis of polymers which might be used in optoelectronic materials and bio-related applications. This method can be easily up scaled and potentially utilized to develop a drug delivery vehicle or multi-stimuli responsive actuator for wide applications.

Data Availability

The data that supports the findings of this study are available in the supplementary material of this article.

CRediT authorship contribution statement

Devendra Kumar: Conceptualization, Methodology, Investigation, Writing – original draft. **Subrata Dolui:** Investigation. **Bhanendra Sahu:** Investigation. **Sanjib Banerjee:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

It contains tables of results, additional analyses including IR spectra and SEC traces. Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111348.

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Phosphorus-containing smart, multifunctional polymers towards materials with dual stimuli responsivity, self-aggregation ability and tunable wettability

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ABSTRACT

A simple, inexpensive and recyclable photo-induced reversible deactivation radical polymerization (RDRP) of a phosphorus-containing monomer, dimethyl(methacryloyloxymethyl) phosphonate (MAPC1) in ionic liquid (without the need for any conventional photoinitiators or dye sensitizers) is developed for the first time to produce low dispersity ($Đ \leq 1.24$) phosphorus-containing polymer, PMAPC1 (at least up to 20200 g mol^{-1}) and a series of well-defined multifunctional PMAPC1-*b*-poly(M) diblock copolymers (where "M" represents polyethylene glycol methacrylate (PEGMA), 2,2,3,3,4,4,5,5-octafluoropentylacrylate (OFPA) and 2-hydroxyethyl methacrylate (HEMA)) thereof. Kinetic monitoring of the photoRDRP of MAPC1 demonstrated good control of the polymerization. Temporal control, catalyst and ionic liquid recyclability of the polymerization was also demonstrated. The synthesized PMAPC1-*b*-PPEGMA diblock copolymers exhibited a dual (pH and temperature) stimuli-responsive behavior. Cloud point of PMAPC1-*b*-PPEGMA diblock copolymers can be tuned by changing the PEGMA mol% in the BCP. Amphiphilic PMAPC1-*b*-PHEMA diblock copolymer undergoes self-aggregation forming spherical nanoobjects. Phosphonate ester moieties of the synthesized diblock copolymers were selectively hydrolyzed to promising PMAPC1(OH)$_2$-*b*-poly(M) diblock copolymers that could be used for many applications, including dual stimuli-responsive materials, materials with tunable hydrophobicity, and self-aggregation ability.

1. Introduction

Phosphorus-containing polymers, due to their unique properties[1], are widely utilized as flame-resistant additives,[2–6] membranes for fuel cells,[7–10] dental adhesives,[11] adhesion promoter,[12–14] hole-transporting materials in OLEDs,[15,16] ion exchange resins,[11] wastewater treatment,[17] superlubricity coatings,[18] anticorrosion coatings,[19] and in the biomedical applications.[20,21] In the last decades, different phosphorus-containing monomers have been developed which includes vinyl,[22] (meth)acrylate[23] and (meth)acrylamide.[23] Phosphorus-containing monomers are primarily polymerized via free radical polymerization (FRP).[20,24,25] However, for emerging applications of phosphorus-containing polymers, synthesis of phosphorus-containing well defined copolymers bearing specific functional groups is needed. In this context, several controlled/living polymerization techniques such as atom transfer radical polymerization (ATRP),[26] single electron transfer-living radical polymerization (SET-LRP),[27,28] reversible addition fragmentation chain transfer (RAFT) polymerization,[29] nitroxide-mediated radical polymerization (NMP),[30] organometallic-mediated radical polymerization[31–33] and living cationic polymerization[34,35] have enabled production of functional polymers appropriate for emerging applications.[36].

Dimethyl(methacryloyloxymethyl) phosphonate (MAPC1) is a unique monomer bearing pendant phosphorus functionality which provides good adhesive and anticorrosive properties.[11,25,37] Reversible deactivation radical polymerization (RDRP) of MAPC1 has been achieved by a few techniques ATRP,[37,38] RAFT,[23] reverse iodine transfer polymerization (RITP)[11] and NMP.[39] However, these processes suffer from the requirement of high polymerization temperature and inability to synthesis well-defined block copolymer. Recently, ionic liquids (ILs), because of their low volatility, wide electrochemical windows, unusual solubilizing properties and possibility of recycling, have gained some interests as a "green" substitute to hazardous organic solvents.[40] ILs are being employed as solvents in RAFT

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Table 1
Polymerization conditions and results for alloy-mediated photoRDRP in ionic liquid.

Entry	Initiator (I)	Monomer	$[M]_o$ $[I]_o$	Time (h)	Conv. (%)	$M_{n,theo}$ [a] (g/mol)	$M_{n,NMR}$ [b] (g/mol)	$M_{n,SEC}$ [c] (g/mol)	$Đ$ [c]
*P*1	EBiB	MAPC1	10	3	100	2300	2450	2800	1.20
*P*2	EBiB	MAPC1	20	3	100	4400	4150	3700	1.22
*P*3	EBiB	MAPC1	40	3	100	8500	8940	8100	1.23
*P*4	EBiB	MAPC1	60	3	100	12,700	13,300	13,800	1.24
P5	EBiB	MAPC1	80	3	100	16,800	16,200	16,100	1.22
*P*6	EBiB	MAPC1	100	3	100	21,000	20,180	20,200	1.21
P7	*P*1	PEGMA	50	3	100	20,450	22,200	23,100	1.22
P8	*P*1	PEGMA	75	3	100	29,450	28,600	30,700	1.24
P9	*P*1	PEGMA	100	3	100	38,450	37,300	40,900	1.25
P10	*P*1	HEMA	50	2	100	8950	8250	10,700	1.23
P11	*P*1	HEMA	75	2	100	12,200	13,100	14,100	1.24
P12	*P*1	HEMA	100	2	100	15,450	16,850	17,400	1.27
P13	*P*1	OFPA	50	6	100	16,750	15,200	18,300	1.23
P14	*P*1	OFPA	75	6	100	23,900	24,350	26,900	1.27
P15	*P*1	OFPA	100	6	100	31,050	32,900	33,000	1.26

[a] Calculated using yield as conversion and the following equation: $M_{n,theo} = ([M]_0/[I]_0 \times \text{yield} \times M_M) + M_I$.

[b] Calculated from DP_{NMR} using equation (3) for PMAPC1-Br and equation (7) for PMAPC1-*b*-poly(M) copolymers.

[c] Obtained from *SEC* measurements, narrow linear poly(methyl methacrylate) standards were used to calibrate the *SEC* instrument.

polymerization,[41] NMP,[42] ATRP[43,44] and SET-LRP[45]. However, the requirement of high polymerization temperature (~ 70 °C) and inefficient chain end-reactivation leading to poorly defined block copolymers restricted their use.[46,47] Additionally, wide industrial adaptability of RDRP could not be achieved because of: (a) inadequate to catalyst recovery process, which resulting toxicity and undesired color in final product (in ATRP),[48] (b) due to S-chain ends there is unwanted odor, color and toxicity (in RAFT polymerization),[49] and (c) in NMP, high polymerization temperature and long polymerization times requirement due to slow polymerization kinetics.[50] Considering the wider potential application of phosphorus-containing polymers, this constraint in the synthesis protocol needs to be overcome.

Recently, the range of RDRP processes has been expanded by the introduction of external stimuli induced RDRP,[51] including pressure,[52] electrochemistry[53] and photochemical irradiation.[54,55] Among them, photoRDRP may offer low environmental pollution, improved spatiotemporal control and molar mass.[56–64] To this end, our group recently reported recyclable Ni-Co alloy nanoparticle mediated ambient temperature RDRP of (meth)acrylate[65,66] and meth (acrylamide)[67,68] monomers and extended this towards the development of recyclable Ni-Co alloy nanoparticle mediated photoRDRP of glycidyl methacrylate in ionic liquid.[69] However, alloy-mediated photoRDRP of any phosphorus-containing monomer in ionic liquid is never reported and if achieved might extend the scope of functional phosphorus-containing polymers. Herein, we report Ni-Co alloy-mediated green and recyclable photoRDRP of MAPC1 in IL (which is also recyclable), producing PMAPC1 and PMAPC1-*b*-poly(M) diblock copolymers (where "M" stands for polyethylene glycol methacrylate (PEGMA), 2,2,3,3,4,4,5,5-octafluoropentylacrylate (OFPA) and 2-hydroxyethyl methacrylate (HEMA)) thereof. The synthesized block copolymers exhibited some interesting properties such as stimuli responsivity, tunable surface hydrophobicity, and self-aggregation ability. Phosphonate ester moieties of the synthesized diblock copolymers were selectively hydrolyzed to unique materials with many potential applications.

2. Experimental

1. Materials

All the chemicals were procured from Sigma-Aldrich, unless stated otherwise. The monomers, 2,2,3,3,4,4,5,5-octafluoropentylacrylate (OFPA, 99 %, Sigma-Aldrich) and 2-hydroxyethyl methacrylate (HEMA, 99%, Sigma-Aldrich) and poly(ethylene glycol) methacrylate (PEGMA, average M_n 360, Sigma-Aldrich) were freed from inhibitors by passing them through a column of basic alumina. PVPh-Ni_3Co_1 alloy nanoparticles[70] were prepared via the reduction of a mixture of Cobalt(II) acetylacetonate ($Co(acac)_2$, 97 %, Sigma-Aldrich) and nickel(II) acetylacetonate ($Ni(acac)_2$, 95 %, Sigma-Aldrich) using hydrazine hydrate ($N_2H_4 \cdot H_2O$, reagent grade, N_2H_4 50–60 %, Sigma-Aldrich) as the reducing agent, following a procedure reported earlier by Mandal and co-workers. 1-butyl-3-methylimidazolium bromide (BMIMBr)[71] and dimethyl(methacryloyloxy)methyl phosphonate (MAPC1)[25] were prepared by following earlier reported procedures.

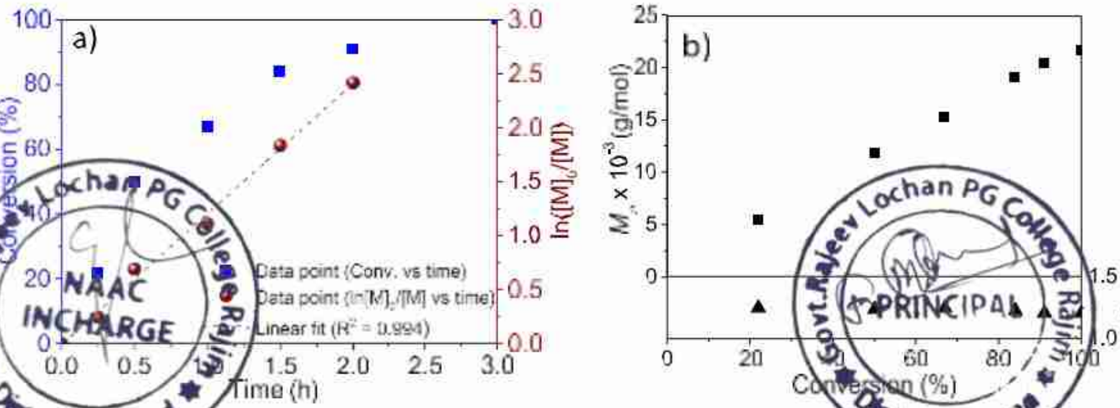

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Fig. 1. Plot of a) conversion (%) and ln([M]$_0$/[M]) vs time and b) evolution of M_n and $Đ$ with conversion for alloy-mediated photoRDRP of MAPC1 in ionic liquid.

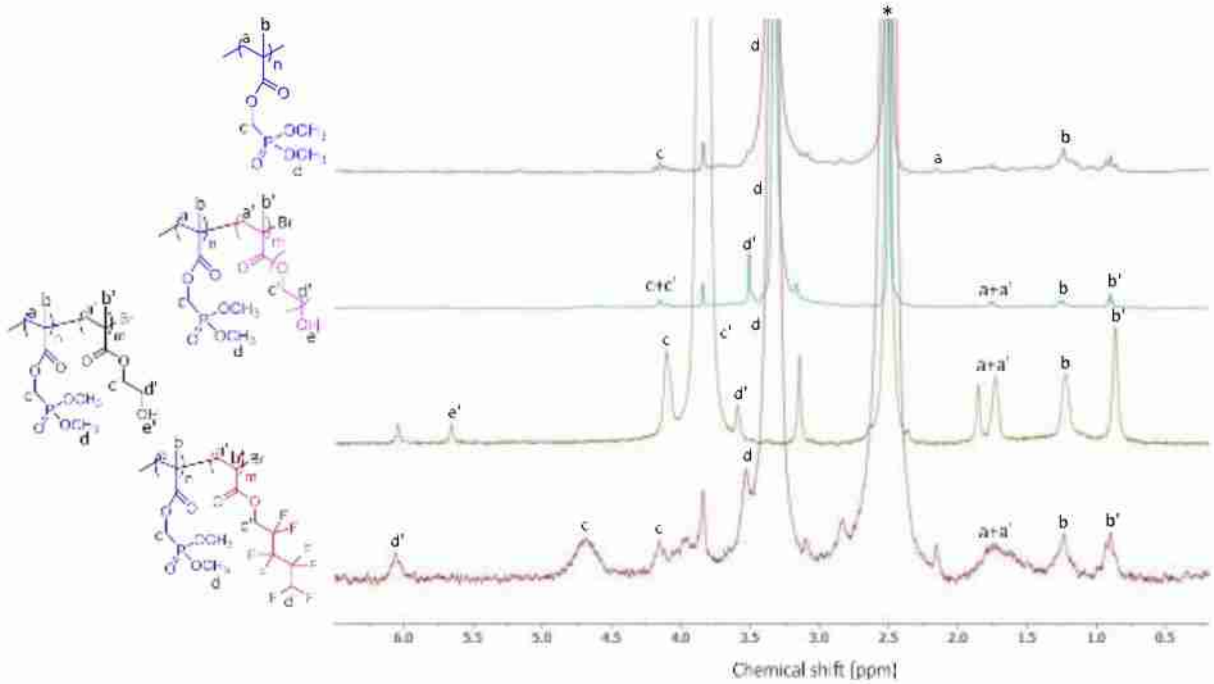

Fig. 2. ^{1}H NMR spectra of PMAPC1$_{10}$-Br (*P*1, Table 1), PMAPC1$_{10}$-*b*-PPEGMA$_{100}$ (P9, Table 1), PMAPC1$_{10}$-*b*-PHEMA$_{100}$ (P12, Table 1) and PMAPC1$_{10}$-*b*-POFPA$_{100}$ (P15, Table 1).

2.2. Alloy-mediated PhotoRDRP of MAPC1 in ionic liquid

Typically, Ni-Co nanoparticle (2 mg, 0.04 mmol), Me$_6$TREN (11 μL, 0.04 mmol), EBiB (6 μL, 0.04 mmol), BMIMBr (0.53 mL) and degassed MAPC1 (1.664 g, 8.0 mmol) were taken in a glass vial. It was then degassed by N$_2$ bubbling, sealed and then irradiated with UVA (λ_{max} = 365 nm) to initiate the polymerization. After a predetermined time, the polymerization was quenched by turning the UVA light irradiation off and the catalyst was separated using a bar magnet and the crude polymer was precipitated into chilled methanol, collected and dried.

^{1}H NMR (400 MHz, DMSO-d_6, δppm of *P*1, Table 1, Fig. 2): 0.9–1.1 ($-CH_2C(C\underline{H}_3)$ of PMAPC1 main chain, signal b), 1.1–1.3 ($-OCH_2C\underline{H}_3$ of the initiator fragment), 1.9–2.2 ($-C\underline{H}_2C(CH_3)$ of PMAPC1, signal a); 3.3–4.1 ($-OC\underline{H}_3$ of PMAPC1, signal d). 4.2–4.4 ($-OC\underline{H}_2-P$, signal c).

The theoretical molar masses ($M_{n,theo.}$) of the polymers were calculated using the following equation:

$$M_{n,theo.} = M_{EBiB} + \left[\frac{[MAPC1]_0}{[EBiB]_0} \times M_{MAPC1} \times \alpha_{MAPC1}\right] \tag{1}$$

where M_{MAPC1} = 208 g mol^{-1}, M_{EBiB} = 195 g mol^{-1}, α_{MAPC1} is the MAPC1 conversion at time *t*.

DP and $M_{n,NMR}$ calculations. For PMAPC1 homopolymers (*P*1-*P*6, Table 1), using ^{1}H NMR spectroscopy,

$$DP\ of\ PMAPC1 = \frac{\frac{1}{2} \times \int_{4.2}^{4.4} -OCH_2-P}{\frac{1}{3} \times \int_{1.1}^{1.3} -OCH_2C\boldsymbol{H}_3} \tag{2}$$

where $\int_i^j CH$ stands for the integral of the signal assigned to CH ranging from *i* ppm to *j* ppm in the ^{1}H NMR spectrum of the polymer.

$$M_{n,NMR} = M_{EBiB} + (M_{MAPC1} \times DP) \tag{3}$$

where M_{MAPC1} and M_{EBiB} stand for the molar masses of MAPC1 (208 g mol^{-1}) and EBiB (195 g mol^{-1}), respectively.

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2.3. Kinetics study of photoRDRP of MAPC1 in ionic liquid

Six polymerization experiments were performed following the protocol described above under UVA irradiation (λ_{max} = 365 nm) and they were quenched at different times (ranging from 15 min to 3 h) to assess the evolution of (i) the monomer conversion and (ii) molar masses (M_ns) and dispersity values (*Đ*s) by gravimetry and *SEC*, respectively.

2.4. Synthesis of PMAPC1 with varying M_ns

PMAPC1 of differing molar masses (DP_n = 10–100) were prepared, by varying [MAPC1]$_0$/[EBiB]$_0$ feed ratio, maintaining other reaction parameters constant, using the protocol described above.

2.5. Catalyst recyclability analysis

After the first set of photoRDRP of MAPC1 in IL, catalyst was separated using a magnetic bar, washed and dried and then used again as catalyst for next set of photoRDRP of MAPC1.

2.6. Ionic liquid recyclability analysis

After the completion of the first reaction of photoRDRP of MAPC1 in IL, the ionic liquid was extracted out of the reaction vessel by dissolving it in methanol and then the PMAPC1-free IL was reused for the next photoRDRP of MAPC1.

2.7. "ON/OFF" light switch reactions

After 15 min of initiating the first reaction of photoRDRP of MAPC1 in IL, the UVA irradiation was turned OFF and the reaction mixture was kept in dark phase (OFF state) for a predetermined time, after which UVA irradiation was again turned ON. The "ON/OFF" experiments were carried out for multiple cycles and during each ON and OFF cycle aliquots were withdrawn to calculate the monomer conversion and the molecular mass and dispersity values.

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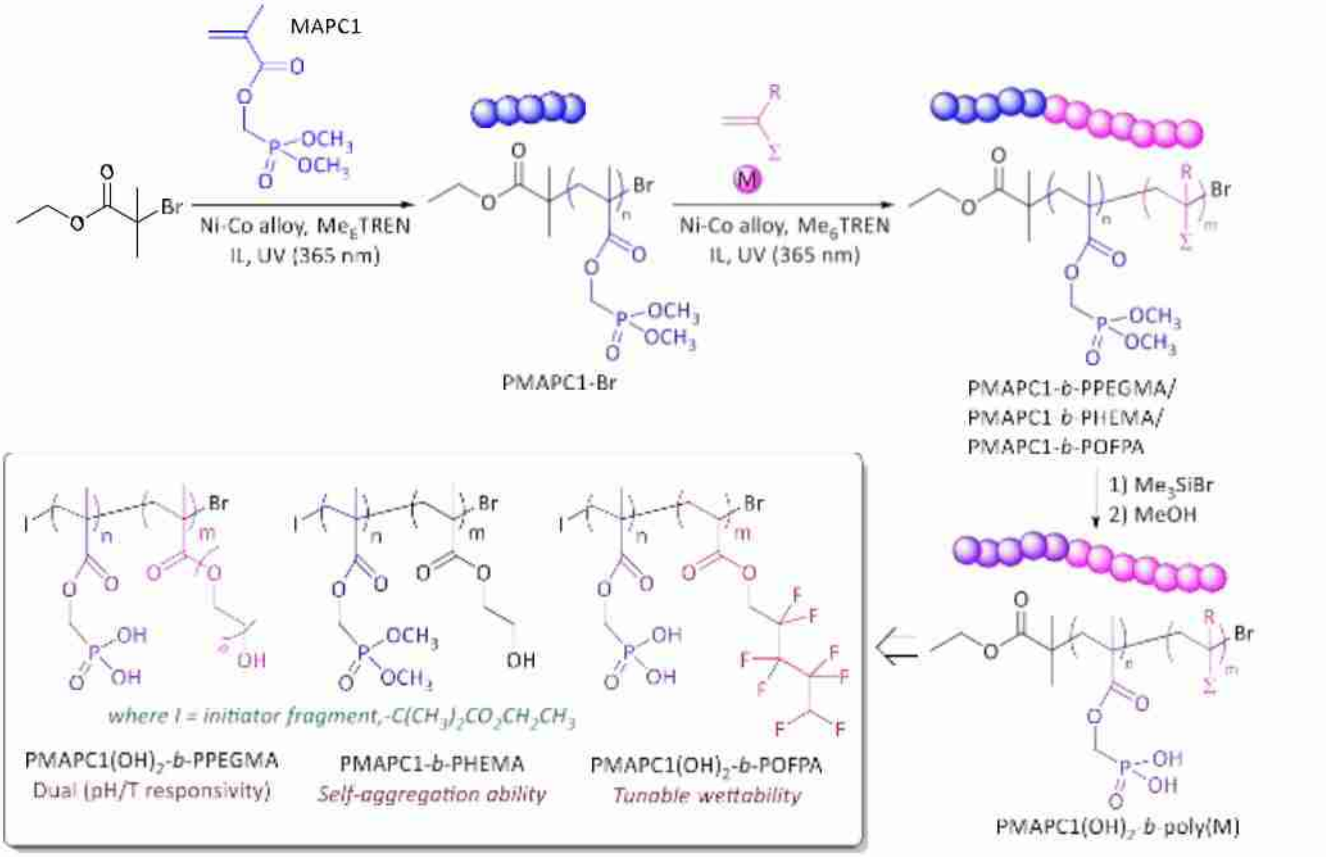

Scheme 1. Synthesis of phosphorus-containing multifunctional polymers.

2.8. *Synthesis of PMAPC1-b-poly(M) diblock copolymers*

Syntheses of PMAPC1-*b*-poly(M) copolymers (where M = PEGMA, HEMA and OFPA) were carried out via alloy-mediated photoRDRP using PMAPC1-Br (*P*1, Table 1) as the macroinitiator following the protocol described above.

^{1}H NMR (400 MHz, DMSO-d_6, δ ppm of P9, Table 1 and Fig. 2): 0.5–0.8 ($-CH_2C(C\underline{H})_3$ of the PEGMA repeat unit, signal b′); 0.9– 1.2 ($-CH_2C(CH_3)$ of MAPC1 repeat unit, signal b); 1.6–2.2 ($-C\underline{H}_2C(CH_3)$ of MAPC1 repeat unit, signal a and $-C\underline{H}_2C(CH_3)$ of PEGMA, signal a′); 3.3–3.6 ($-OC\underline{H}_3$ of MAPC1 repeat unit, signal d and $-OCH_2C\underline{H}_2$ of PEGMA, signal d′); 3.9–4.3 ($-OC\underline{H}_2-P$ of MAPC1 repeat unit, signal c and $-OC\underline{H}_2CH_2$ of PEGMA repeat unit, signal c′).

DP and $M_{n,NMR}$ calculations. For PMAPC1-*b*-poly(M) block copolymers (P7-P15, Table 1), using ^{1}H NMR spectroscopy,

$$DP\ of\ PMAPC1-b-PPEGMA = \frac{\frac{1}{3}\times\int_{0.5}^{0.8}-CCH_3}{\frac{1}{3}\times\int_{0.9}^{1.2}-CCH_3}\times DP_{PMAPC1-Br} \tag{4}$$

$$DP\ of\ PMAPC1-b-PHEMA = \frac{\frac{1}{2}\times\int_{3.6}^{3.8}-OCH_2}{\frac{1}{2}\times\int_{4.0}^{4.3}-OCH_2}\times DP_{PMAPC1-Br} \tag{5}$$

$$DP\ of\ PMAPC1-[illegible] = \frac{\frac{1}{2}\times[illegible]-OCH_2}{\frac{1}{2}\times\int_{4.0}-OCH_2}\times DP_{PMAPC1-Br} \tag{6}$$

$$M_{n,NMR} = M_{PMAPC1-Br} + (M_M\times DP) \tag{7}$$

where $M_{PMAPC1-Br}$ and M_M represents the molar masses of PMAPC1-Br (2450 g mol^{-1}) and PEGMA (360 g mol^{-1}) or HEMA (130 g mol^{-1}) or OFPA (286 g mol^{-1}), respectively.

2.9. *Synthesis of phosphonic acid-functionalized PMAPC1(OH)$_2$-b-poly (M)*

Hydrolysis of dimethylphosphonate ester groups of PMAPC1-*b*-poly (M) diblock copolymers were carried out using bromotrimethylsilane at room temperature by following an earlier report by McKenna et al.[72] Typically, PMAPC1-*b*-PPEGMA (P9, Table 1) was dissolved in anhyd. DCM under N_2 atmosphere and treated with bromotrimethylsilane. After that, the reaction mixture was treated with methanol and the polymer was collected by centrifugation and dried to obtain the hydrolyzed product.

2.10. *Aggregation procedure*

Typically, the as-synthesized and purified PMAPC1-*b*-PHEMA (5 mg) was dissolved in 1 mL water and was kept in a closed vial.

2.11. *Dye uptake procedure*

In a typical process, 3 mg of PMAPC1-*b*-PHEMA copolymer was added to Coumarin 102 (C102) solution (3 mL) and allowed to stand undisturbed for 12 h. During this time, the amount of dye uptake was monitored by UV–vis Spectroscopy via changes in the C102 absorbance. Finally, the C102 incorporated polymers were isolated by centrifugation and washed to get rid of any physically adsorbed C102 dye. Finally, the dye-loaded polymer nanospheres were dispersed in water and analyzed by fluorescence spectroscopy and fluorescence microscopy technique.

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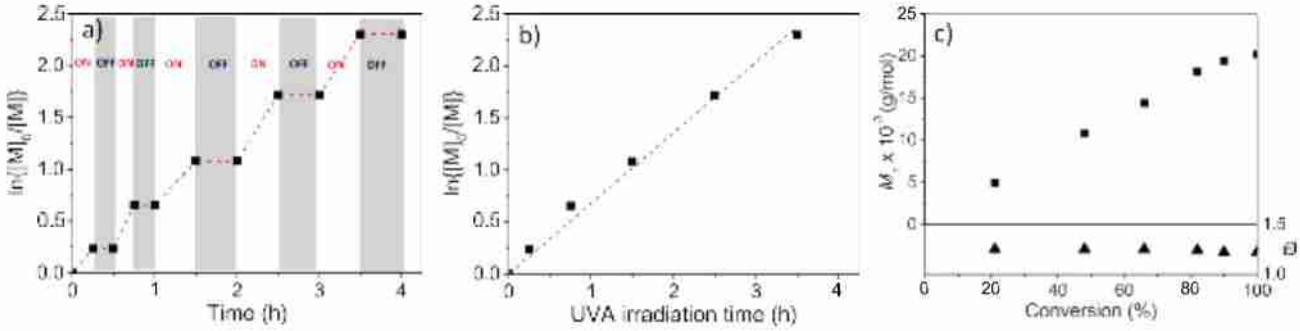

Fig. 3. Temporal control for photoRDRP of MAPC1 in ionic liquid. Plot of a) ln([M]$_0$/[M]) vs time, b) ln([M]$_0$/[M]) vs UVA irradiation time and c) evolution of M_n and Đ vs monomer conversion.

2.12. Method for polymer coating

Typically, PMAPC1(OH)$_2$-*b*-POFPA copolymer solution was deposited onto glass plates using a BarCoater.

2.13. Characterization

The chemical structure of the products were determined by NMR (Bruker 400 MHz spectrometer) at 25 °C. IR spectra are recorded on a Perkin Elmer Spectrum 100 with a diamond crystal, using 16 scans per spectrum and a resolution of 4 cm^{-1}. Molar masses (M_ns) and dispersities (Đs) were determined by a size exclusion chromatography (*SEC*) (from Agilent Technologies) using a PL0390-0605390 LC light scattering detector capable of detecting at two diffusion angles (15° and 90°), a PL0390-06034 capillary viscometer, a 390-LC PL0390-0601 refractive index detector and two PL1113-6300 ResiPore 300 × 7.5 mm columns thermostated at 35 °C in DMF (containing 0.1 wt% of LiCl) as the eluent at a flow rate of 0.8 mL min^{-1}. The entire *SEC* system was thermostated at 35 °C and narrow linear poly(methyl methacrylate) standards with peak molecular weights (M_p) ranging from 600 g mol^{-1} to 100000 g mol^{-1} were used to calibrate the *SEC* instrument. TGA was performed using a Netzsch TG 209 F3 instrument, at a heating rate of 10 °C min^{-1} in N_2 atmosphere. Temperature responsiveness of the aqueous solution of PMAPC1(OH)$_2$-*b*-PPEGMA diblock copolymers were measured on a Shimadzu UV-2600 spectrophotometer equipped with a temperature-controlled sample holder. The transmittance of the polymer solution was monitored in the temperature range of 10 to 80 °C at a detection wavelength of 500 nm, at a heating rate of 1 °C min^{-1}. FESEM analysis was performed using Zeiss Gemini SEM500 at an accelerating voltage of 5 kV. TEM analysis of the Ni-Co alloy nanoparticles' suspension in ethanol was performed using a JEOL Transmission Electron Microscope (TEM) (Model JEM-2100F) at an accelerating voltage of 200 kV. Hydrodynamic diameter (D_h) of the polymer solutions were determined using a Malvern Zetasizer (Zetasizer NANO ZS90). Water Contact Angle (WCA) measurements of the polymer thin films were carried out using a Contact Angle System OCA-Data Physics goniometer using the water sessile drop method. Photoluminescence (PL) spectra of the samples were recorded in a Fluorolog FL3-211 (HORIBA Scientific) with a 450-Watt Xenon arc lamp. Fluorescence microscopy images were recorded using a light microscope (DM2700M, Leica).

3. Results and discussion

1. Alloy-mediated photoRDRP of MAPC1 in ionic liquid

Initial trials to achieve alloy-mediated controlled photopolymerization of the phosphorus-containing monomer, MAPC1 in a room temperature ionic liquid (IL), BMIMBr, revealed that (Table S1, see the Supporting Information) optimum result is obtained using EBiB initiator and Me$_6$TREN ligand upon irradiation with UVA (λ_{max} = 365 nm, Scheme 1). PVPh-Ni$_3$Co$_1$ alloy nanoparticles exhibited spherical morphology as revealed by TEM with an average diameter of 24 nm (Fig. S1). Detailed kinetics study of the polymerization established typical features of RDRP process such as linear dependency of ln([*M*]$_0$/[M]) vs time (Fig. 1a), a linear growth of M_n with conversion (retaining low Đ values) (Fig. 1b). Controlled nature of the polymerization was further demonstrated by the synthesis of low dispersity PMAPC1s of varying M_ns (up to 20200 g mol^{-1}), preserving low Đ values (≤1.24) (Fig. S2 and Table 1).

PMAPC1 was characterized using NMR (Fig. 2) and IR (Fig. S5) spectroscopy. The ^{1}H NMR spectrum of the synthesized PMAPC1 exhibited the typical signals of MAPC1 at 0.9–1.1 (-CH$_2$C(C$\underline{H}_3$) of PMAPC1 main chain, signal b), 1.6–2.2 (-C$\underline{H}_2$C(CH$_3$) of PMAPC1, signal a); 3.3–4.1 (-OC$\underline{H}_3$ of PMAPC1, signal d) and 4.2–4.4 ppm (-OC$\underline{H}_2$-P, signal c).[23,73].

The possibility of temporal control is a key feature of any photopolymerization. Thus, temporal control of the photoRDRP of MAPC1 was investigated by reversibly activating/deactivating the photoRDRP by turning the UVA irradiation ON or OFF. A linear rise of ln([M]$_0$/[M]) vs UVA irradiation time (Fig. 3b) and a linear growth of M_n vs conversion (Fig. 3c) were observed under "ON" state. Notably, no monomer conversion was detected when the UVA irradiation was switched off ("OFF" period), suggesting formation of "dormant" species in the "OFF" period. Successful conduction of multiple "ON"/"OFF" cycles established an excellent temporal control on the polymerization.

Recyclability of the catalyst and IL are important features to establish the true recyclability of the polymerization. Results (Table S2) of the catalyst recyclability study revealed that catalyst efficiency remains intact even after three polymerization cycles. Results of the IL recyclability study (Table S3) show that recycled IL also led to controlled polymerization and synthesis of well-defined PMAPC1s.

3.2. Syntheses of PMAPC1-b-poly(M) diblock copolymers

A range of PMAPC1-*b*-poly(M) block copolymers (BCPs) were synthesized using PMAPC1-Br as the macroinitiator via recyclable alloy-mediated photoRDRP and polyethylene glycol methacrylate (PEGMA) or 2,2,3,3,4,4,5,5-octafluoropentylacrylate (OFPA) or 2-hydroxyethyl methacrylate (HEMA) as the monomer (Scheme 1, Table 1 and Table S4). Narrow unimodal *SEC* traces of the BCPs (Fig. S4) exhibiting clear shifts towards higher molar masses, showing little/no remaining PMAPC1-Br macroinitiator, indicates effective preparation of the BCPs.

^{1}H NMR spectra of the PMAPC1-*b*-poly(M) BCPs reveal the existence of characteristic signals of the PMAPC1 block and the conforming second block PPEGMA or POFPA or PHEMA. Typically, ^{1}H NMR spectrum of the PMAPC1$_{10}$-*b*-PPEGMA$_{100}$ BCP (P9, Table 1) displays the distinguishing signals of the PMAPC1[23,73] first block and PPEGMA [69,74] second block at 0.5–0.8 (-CH$_2$C(C$\underline{H}_3$) of the PEGMA repeat unit, signal b′); 0.9–1.2 (-CH$_2$C(C$\underline{H}_3$) of MAPC1 repeat unit, signal b); 1.6–2.2 (-C$\underline{H}_2$C(CH$_3$) of MAPC1 repeat unit, signal a and -C$\underline{H}_2$C(CH$_3$) of

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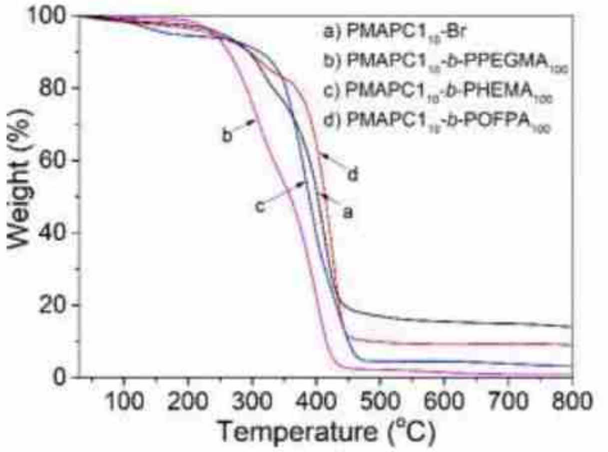

Fig. 4. TGA thermograms of PMAPC1$_{10}$-Br (*P*1, Table 1), PMAPC1$_{10}$-*b*-PPEGMA$_{100}$ (P9, Table 1), PMAPC1$_{10}$-*b*-PHEMA$_{100}$ (P12, Table 1) and PMAPC1$_{10}$-*b*-POFPA$_{100}$ (P15, Table 1).

PEGMA, signal a′); 3.3–3.6 (–OC$\underline{H}_3$ of MAPC1 repeat unit, signal d and –OCH$_2$C$\underline{H}_2$ of PEGMA, signal d′); 3.9–4.3 (–OC$\underline{H}_2$–P of MAPC1 repeat unit, signal c and –OC$\underline{H}_2$CH$_2$ of PEGMA repeat unit, signal c′).

IR spectral analysis (Fig. S5) also establish the structure of the PMAPC1-*b*-poly(M) BCPs. IR spectra (Fig. S5) of PMAPC1$_{10}$-*b*-PPEGMA$_{100}$ (P9, Table 1), PMAPC1$_{10}$-*b*-PHEMA$_{100}$ (P12, Table 1) and PMAPC1$_{10}$-*b*-POFPA$_{100}$ (P15, Table 1) copolymers exhibited a characteristic absorption band corresponding to the PMAPC1 block are at 1025, 1144, 1240, and 1723 cm^{-1} attributed to the P–O–C stretching, P–C–O stretching, P–O and C–O of the ester group respectively,[75] PEGMA block at 860, 946, 1097, 1247, 1447, 2868 and 3453 cm^{-1} corresponding to –CH$_2$-O, C–O–C, *sym.* –CH$_2$, *asym.* –CH$_2$, –CH$_2$ str. and –OH str., respectively,[76] PHEMA block at 1149, 1723, 2941 and 3600–3250 cm^{-1} corresponds to C–O, C–O, –CH$_2$ and –OH str., respectively[77,78] and POFPA block are at 749, 805 and 1447 cm^{-1} corresponds to –CH$_2$, -CF$_2$ and *asym.* –CH$_2$ str. respectively.[66,79].

Thermal properties of the PMAPC1-*b*-poly(M) BCPs were assessed by TGA (Fig. 4). Results showed that compared to PMAPC1, PMAPC1-*b*-POFPA and PMAPC1-*b*-PHEMA are thermally stable more while PMAPC1-*b*-PPEGMA is thermally less stable (Fig. 4). Enhanced thermal stability of the PMAPC1-*b*-POFPA BCP is attributed to the presence of multiple C–F bonds in that BCP.[80].

3.3. Synthesis of phosphonic acid functionalized PMAPC1(OH)$_2$-b-poly (M) copolymers

Hydrolysis of the phosphonate ester groups of PMAPC1-*b*-poly(M) BCPs using bromotrimethylsilane led to the synthesis of phosphonic acid functionalized PMAPC1(OH)$_2$-*b*-poly(M) BCPs. The presence of dimethyl phosphonate ester group in PMAPC1 copolymer was further proved by the IR spectrum by the frequencies for ester P–O stretching at 1240 cm^{-1} and P–O–C str. bands at 1025 cm^{-1} (Fig. S5).[7,81,82] The successful complete hydrolysis of such a phosphonate ester was confirmed by the disappearance of the P–O–C stretching bands and the appearance of O–H stretching frequency (Fig. S6). ^{1}H NMR spectra of the hydrolyzed PMAPC1(OH)$_2$-*b*-poly(M) BCPs (Fig. 5) revealed the disappearance of the signal corresponding to the –OCH$_3$ group of the dimethylphosphonate ester of PMAPC1-*b*-poly(M) BCPs, suggesting successful synthesis of the phosphonic acid functionalized BCPs.[10].

^{19}F NMR spectrum of the [PMAPC1(OH)$_2$]$_{10}$-*b*-POFPA$_{100}$ BCPs (Fig. S7) revealed the presence of peaks corresponding to the four different types of –CF$_2$ groups of the POFPA segment.[83] Successful hydrolysis of the phosphonate ester moiety of PMAPC1$_{10}$-*b*-POFPA$_{100}$ (P15, Table 1) to [PMAPC1(OH)$_2$]$_{10}$-*b*-POFPA$_{100}$ (hydrolyzed product of P15, Table 1) was further confirmed via ^{31}P NMR analysis (Fig. S8).

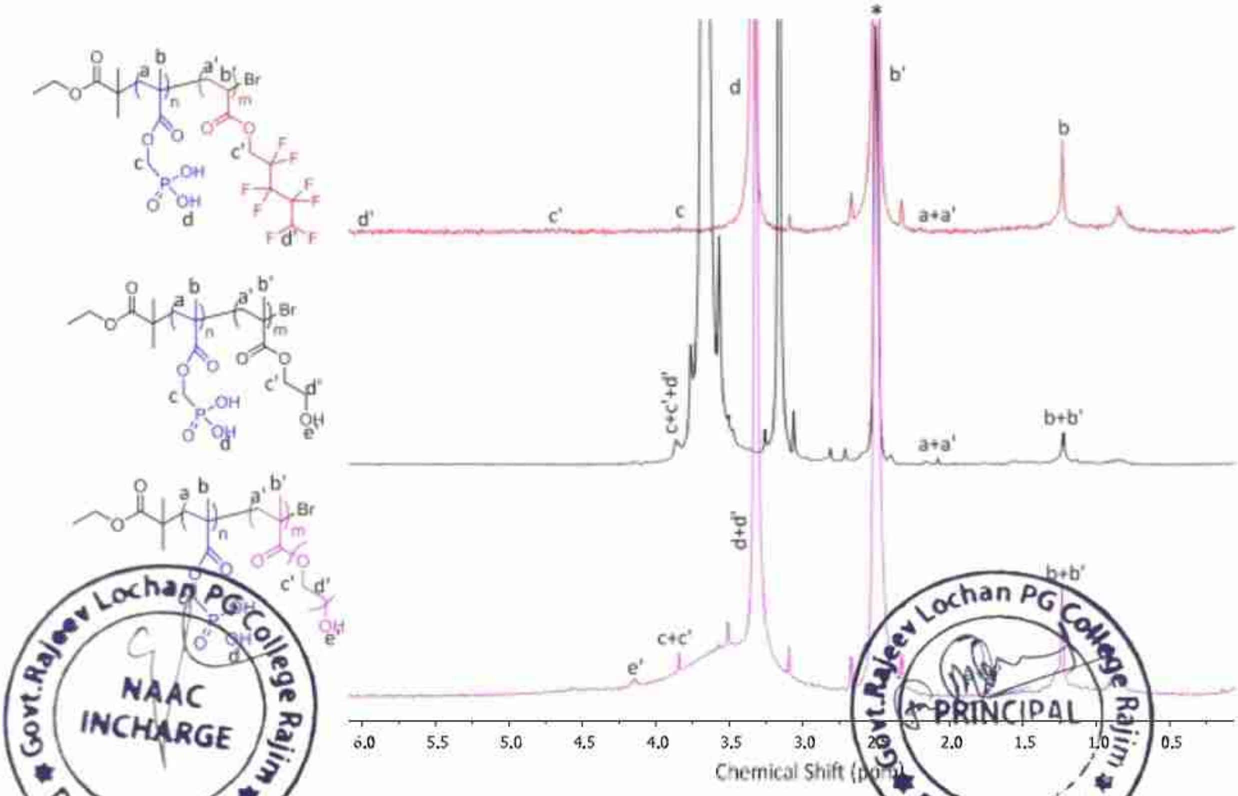

Fig. 5. ^{1}H NMR spectra of [PMAPC1(OH)$_2$]$_{10}$-*b*-PPEGMA$_{100}$ (hydrolyzed product of P9, Table 1), [PMAPC1(OH)$_2$]$_{10}$-*b*-PHEMA$_{100}$ (hydrolyzed product of P12, Table 1) and [PMAPC1(OH)$_2$]$_{10}$-*b*-POFPA$_{100}$ (hydrolyzed product of P15, Table 1).

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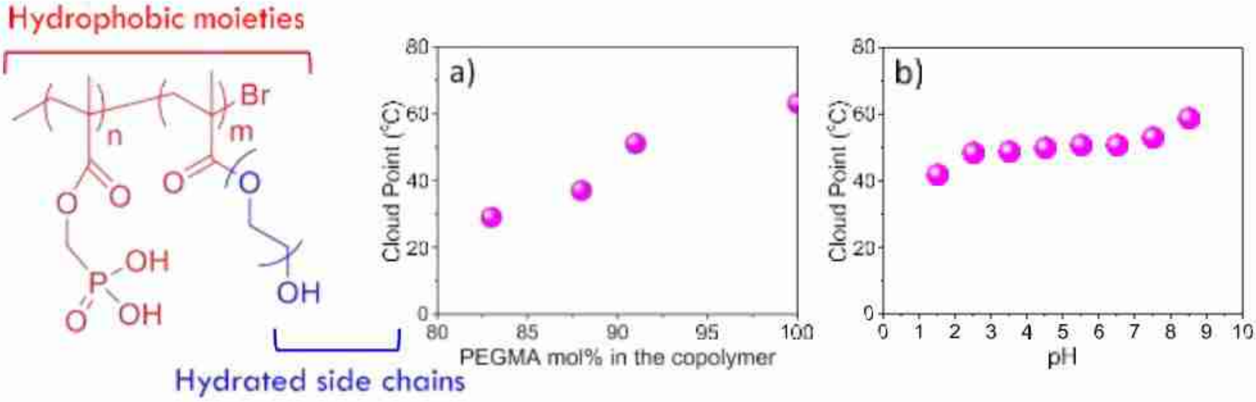

Fig. 6. (a) Evolution of T_{CP} vs PEGMA content in PMAPC1(OH)$_2$-*b*-PPEGMA BCPs. (b) T_{CP} as a function of solution pH for [PMAPC1(OH)$_2$]$_{10}$-*b*-PPEGMA$_{100}$ BCP.

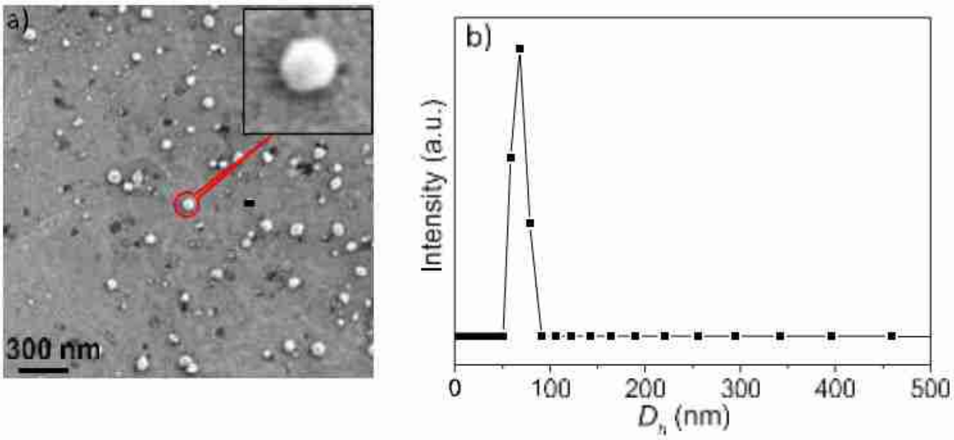

Fig. 7. (a) FESEM image of the PMAPC1$_{10}$-*b*-PHEMA$_{100}$ aggregates and (b) Size distributions of the PMAPC1$_{10}$-*b*-PHEMA$_{100}$ nano aggregates by DLS.

3.4. *pH and temperature response of PMAPC1(OH)$_2$-b-PPEGMA diblock copolymers*

Phosphonic acid functionalized PMAPC1(OH)$_2$-*b*-PPEGMA BCPs were expected to display pH and temperature responsiveness because of the properties of PMAPC1(OH)$_2$[84,85] and PPEGMA[86] segments, respectively. Cloud point (T_{CP}) of PPEGMA homopolymer was estimated to be 63 °C,[87] whereas that of PMAPC1(OH)$_2$-*b*-PPEGMA BCPs (measured in aqueous solution) decreased to 29 °C, with rise of PMAPC1 (OH)$_2$ block in the copolymer (Table 1 and Fig. 6a) at pH 6.5. T_{CP} of [PMAPC1(OH)$_2$]$_{10}$-*b*-PPEGMA$_{100}$ changes from 42 to 59 °C upon changing the pH of the solution from 1.5 to 8.5 (Fig. 6b). Both heating and cooling measurements were performed and the process was reversible. This result establishes that pH has an impact on T_{CP} of the BCPs. Deprotonation of both the -OH groups of the PMAPC1(OH)$_2$ segments at higher pH (pH ≥ 7.5) resulted in more hydrophilicity (reported pKa1 and pKa2 of phosphoric acid are 2.1 and 7.2, respectively) and increase in the T_{CP} value (Fig. 6b).[84,85].

3.5. *Self-aggregation behavior of PMAPC1-b-PHEMA diblock copolymers*

The amphiphilic PMAPC1$_{10}$-*b*-PHEMA$_{100}$ BCP, consisted of hydrophobic PMAPC1 and hydrophilic PHEMA block, undergoes self-aggregation into spherical nanomaterials at pH 7.0, as revealed by DLS (Fig. 7b, D_h = 6[illegible] nm) and FESEM (Fig. 7a, D_{FESEM} = 60 ± 20 nm) when used at a concentration of 5 mg/mL. The effect of PMAPC1$_{10}$-*b*-PHEMA$_{100}$ BCP concentration on the self-aggregation was also studied.

Results (Fig. S[illegible]) revealed that at a lower (2 mg/mL) and higher (10 mg/mL) concentration also the copolymer self-aggregates into spherical nanomaterials with D_{FESEM} = 66 ± 30 nm (D_h = 146 nm) and D_{FESEM} = 74 ± 36 nm (D_h = 197 nm), respectively. However, the double hydrophilic PMAPC1(OH)$_2$-*b*-PHEMA BCP, obtained via hydrolysis of the dimethylphosphonate ester groups of PMAPC1-*b*-PHEMA BCP, does not exhibit any self-aggregation.

To have further understanding of the aggregation process, incorporation of coumarin 102 (C102, a representative hydrophobic dye) into the hydrophobic core of the aggregated micro/nanospheres during the aggregation of PMAPC1-*b*-PHEMA was investigated. C102 absorbance (at 395 nm) reduced steadily with time (Fig. 8a) leading to ~ 97 % dye encapsulation after 24 h (Fig. 8b).

The fluorescence emission spectrum of PMAPC1-*b*-PHEMA (Fig. 8c) with encapsulated C102 was of reduced intensity than that of solution containing neat C102, indicating encapsulation of C102. Fluorescence light microscopic image (Fig. 8d) depicts green light-radiating beads of PMAPC1-*b*-PHEMA BCPs with encapsulated C102, validating dye encapsulation inside the pores of PMAPC1-*b*-PHEMA BCP.

3.6. *Surface properties of PMAPC1(OH)$_2$-b-POFPA diblock copolymers*

Surface properties of the PMAPC1(OH)$_2$-*b*-POFPA BCP thin films coated on glass slide were studied by means of WCA measurements (Fig. 9). Neat PMAPC1(OH)$_2$ film was hydrophilic (WCA = 55°). WCA measurements indicated that increase in OFPA (which contain multiple F atoms) content in the PMAPC1(OH)$_2$-*b*-POFPA BCP films caused an increase of the film hydrophobicity (Fig. 9). This is in accordance with the literature reports which described that incorporation of the fluorinated moieties in the BCP increases the WCA.[88]

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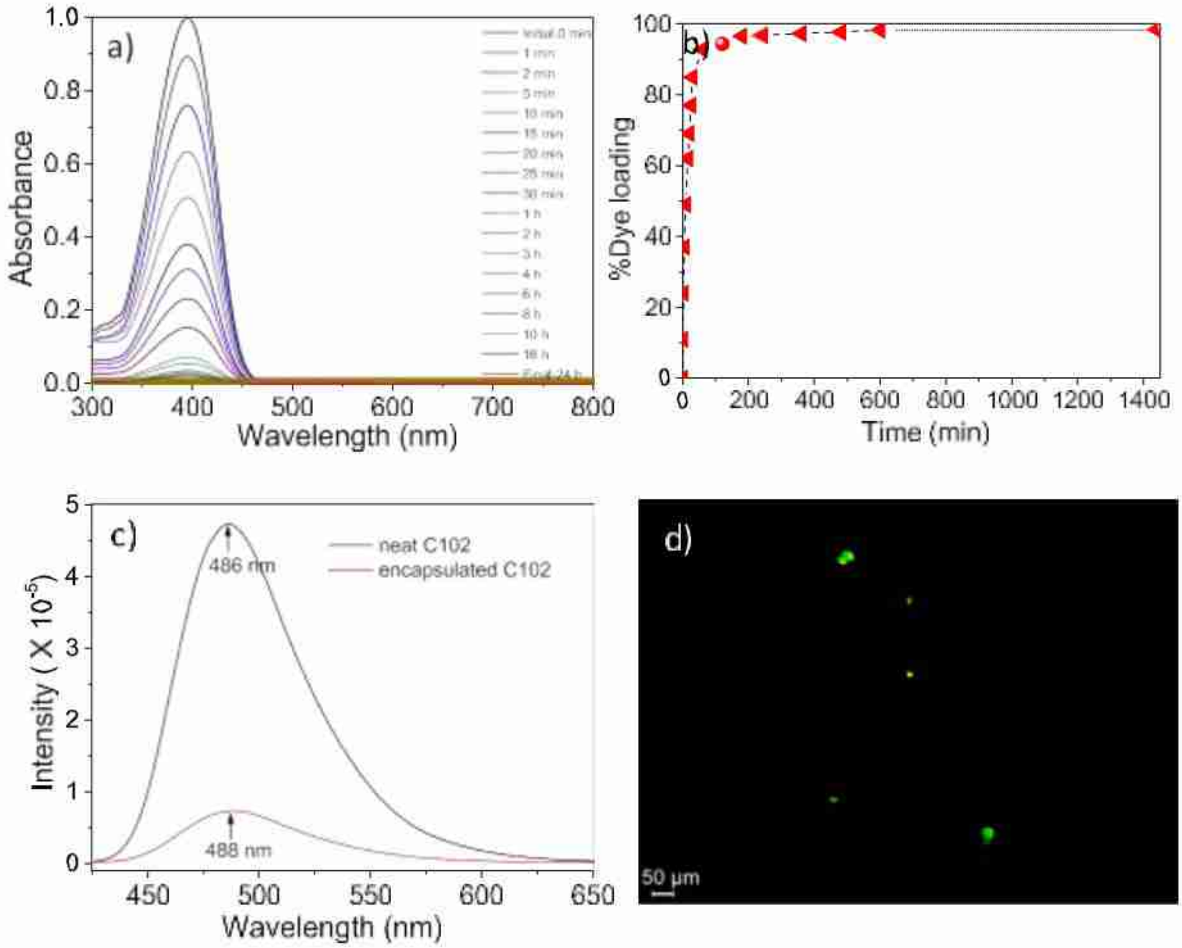

Fig. 8. (a) Time dependent UV–vis spectra, (b) %Dye loading vs time, (c) fluorescence emission spectra and (d) fluorescent light microscopy image during dye encapsulation experiment.

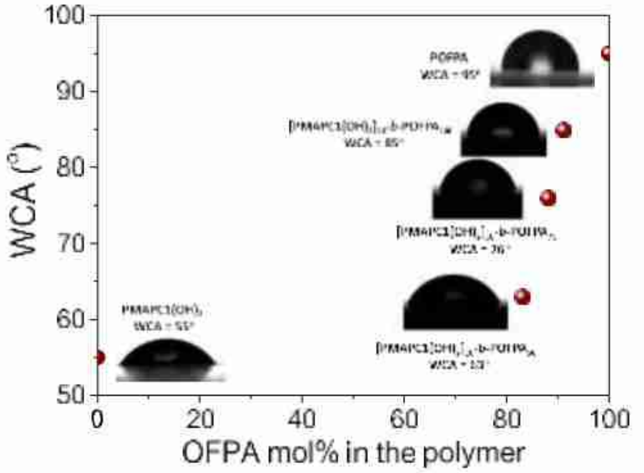

Fig. 9. Variation of WCAs vs OFPA content for PMAPC1(OH)$_2$-*b*-POFPA copolymer films and images of corresponding water droplets.

Remarkably, the [PMAPC1(OH)$_2$]$_{10}$-*b*-POFPA$_{100}$ BCP film containing high amounts (91 mol%) of OFPA (P15, Table 1) was hydrophobic (WCA = 85°). Notably, WCA of a reference POFPA homopolymer sample coated on glass slide was 95°. The above result revealed that by controlling the OFPA amount in the copolymer, wettability[66,89–91] of the BCP surface can be tuned.

4. Conclusions

In summary, for the very first time, we present synthesis of smart, multifunctional diblock copolymers for applications as materials with dual-stimuli responsivity (PMAPC1(OH)$_2$-*b*-PPEGMA), self-aggregation ability (PMAPC1-*b*-PHEMA) and tunable wettability (PMAPC1(OH)$_2$-*b*-POFPA) via alloy-mediated recyclable photoRDRP in a "green" solvent-ionic liquid. By varying the nature of the second monomer, three different PMAPC1-*b*-poly(M) BCPs demonstrating dual (pH/temperature) stimuli responsive behavior and tunable cloud point (PMAPC1-*b*-PPEGMA BCP), self-aggregation forming spherical nanoobjects (PMAPC1-*b*-PHEMA BCP) for potential applications in drug delivery and phosphonic acid-functionalized poly(fluoroacrylate)s, PMAPC1(OH)$_2$-*b*-POFPA exhibited tunable wettability were developed. Considering the prevalent interest in multifunctional polymers for electronics, sustainability and health, we predict that the process and materials developed in this work may open new opportunities for photoregulated production of tailored functional polymers.

CRediT authorship contribution statement

Devendra Kumar: Conceptualization, Methodology, Investigation, Writing – original draft. **Bhanendra Sahu:** Investigation. **Sk Arif Mohammad:** Investigation. **Sanjib Banerjee:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that supports the findings of this study are available in the supplementary material of this article.

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***Data** Availability.*

The data that supports the findings of this study are available in the supplementary material of this article.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2022.111646.

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One-Dimensional Polymeric Nanocomposites: Current State-of-the-Art

Sk Arif Mohammad, Devendra Kumar, and Sanjib Banerjee

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1. Introduction

1. Carbon Nanotube-Strengthened Polymer Composites

Carbon nanotubes (CNTs) possess fascinating electrical conductivity and mechanical properties. In 1991, Iijima [1] first reported CNTs. There are two kinds of CNT: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Ajayan *et al.* [2] reported on CNT/epoxy nanocomposites with improved electrical and mechanical properties. The electrical/mechanical properties of these composites are affected by purity, integrity, concentration, and dispersion of CNTs, and polymer types. In the following sections, the synthesis of various CNT-polymeric nanocomposites (PNCs) and their properties will be discussed.

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1. Thermoset Polymer Composites

CNTs tend to self-aggregate, diminishing the full potential of the CNT/PNCs. Hence, there has been a lot of research into improving the dispersibility of CNT/PNCs, using commonly used surfactants like sodium dodecyl sulfate (SDS), poly(phenylene ethynylene)s (PPEs), polystyrene sulfate (PSS), and sodium dodecylbenzene sulfonate (SDBS) (Figure 2.1), as well as *via* attachment of appropriate chemical functionalities. Mei *et al.* [3] synthesized a CNT/epoxy composite with moderate conductivity *via* an ice templating approach.

1. Polyurethane-Based Matrix

Thermoplastic polyurethane (TPU) is composed of a hard segment (composed of aromatic/aliphatic isocyanates) and a soft segment (composed of polyether/polyester polyol). Because of this wide range of physical properties, which are tunable based on the hard/soft segment ratio, TPU is the desired candidate for preparing CNT/PNCs with unique features. To this end, Yakovlev *et al.* [5] achieved the preparation of a CNT/TPU composite with a much-reduced percolation threshold (Figure 2.2).

2. Matrix Based on Polycarbonate or Polyamide-6

Polycarbonate (PC) and polyamide-6 (PA-6) are extensively employed as thermoplastic polymers due to their high chemical, mechanical, and abrasion resistance, along with their thermal, optical, and dimensional stabilities. However, CNT/PC and CNT/PA-6 nanocomposites suffer from insufficient CNT dispersibility. To improve the performance of such nanocomposites, surface modification of CNT is a viable option. The Babal group [6] synthesized MWCNT/PC composites in the presence of a low concentration of filler with a twin-screw extruder with a reverse flow channel.

3. Polyethylene-Based Matrix

Polyethylene (PE) is one of the widely used polymers. Based on the density and branching, PE is classified into linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and ultrahigh molecular weight polyethylene (UHMWPE). Due to its excellent moisture resistance, mechanical, chemical, and tribological qualities, UHMWPE is an excellent choice for application in the nanocomposite field. Such CNT/PE nanocomposites are prepared via dry mixing, ball milling combined with hot pressing, sintering, and blown film extrusion.

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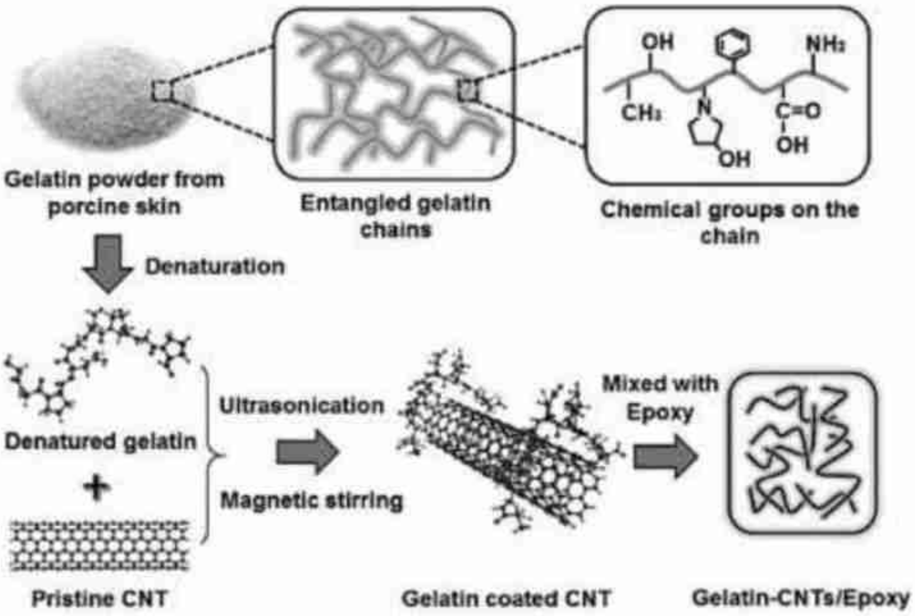

FIGURE 2.1
The creation of a gelatin-CNT/epoxy nanocomposite is depicted. Adapted with permission from Reference [4], Copyright (2018), Elsevier.

4. *Polypropylene-Based Matrix*

Unique thermal, chemical, mechanical, dielectric, and optical properties of polypropylene (PP) make it suitable for application in the automotive, medical, construction, and toy industries. Extrusion/injection molding and hot pressing are the most typical methods for fabricating CNT/PP composites, which exhibit appreciable electrical conductivity (Figure 2.3) [7].

5. *Polystyrene-Based Matrix*

Because of its low production cost, excellent mechanical qualities, and high chemical stability, polystyrene (PS) is commonly used in a wide range of consumer products, such as commercial packaging, bags, cups, and dishes. Injection molding, hot pressing, casting, or spin coating are typical manufacturing processes for CNT/PS composites. However, most of these techniques require sonication, which might affect the physicochemical properties of such composites.

6. *Polymethacrylate-Based Matrix*

Poly(methylmethacrylate) (PMMA) is a good alternative to polycarbonate and glass because of its transparency, excellent mechanical properties, and low weight. As with other thermoplastic polymer-based nanocomposites, the most important hurdle to overcome is how to produce a nanofiller dispersion in a suitable matrix. Apart from the well-known latex method, the functionalization of such nanocomposites may greatly improve the electrical and mechanical performance of the composite. The Koysuren group [9] utilized a chemical vapor deposition (CVD) approach to coat CNTs with non-covalent poly(glycidyl methacrylate) (PGMA), considerably improving the nanofiller–matrix interaction.

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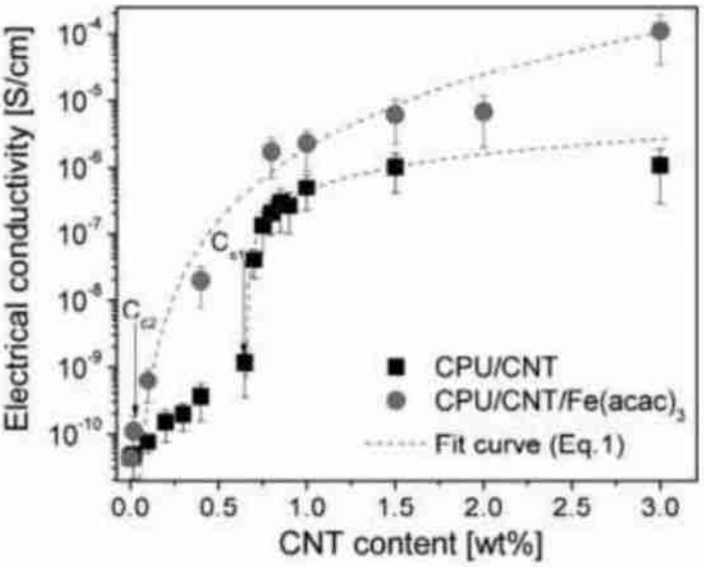

FIGURE 2.2
Electrical conductivity of complex polyurethane (CPU)/CNT and CPU/CNT/Fe(acac)$_3$ composites *vs.* filler weight fraction (a) and a log-log plot of σDC *vs.* C-Cc for the same composites (b). Adapted with permission from Reference [5], Copyright (2017), Elsevier.

2.1.1.1.7 Polymer Composites Strengthened by Carbon Nanofibers

Carbon nanofiber (CNF) is another one-dimensional (1D) carbon nanofiller that is commonly employed. CNF's active carbon atoms are visible on the materials' exterior surface, increasing its chemical reactivity. Ultrasonication, mechanical stirring, solvent casting, and other solution mixing methods are used to prepare CNF-polymer composites. Nie *et al.* [10] reported that silanization of CNFs with (3-aminopropyl)triethoxysilane increased the composite's tensile strength while lowering its electrical conductivity by several magnitudes. Guadagno *et al.* [11] reported that high-temperature heating improved the stiffness and surface smoothness of the material, increasing electrical conductivity and lowering the percolation threshold.

2. Synthesis of One-Dimensional Polymeric Nanocomposites

1. Synthesis Via Electrospinning Technique

Zhang *et al.* [12] prepared a series of unaligned $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$–$0.5(Ba_{0.7}Ca_{0.3})TiO_3$-poly(vinylidene fluoride) (BZCT-PVDF) and aligned BZCT-PVDF and BZCT@SiO_2-PVDF composites *via* a combination of electrospinning and hot-pressing. Finally, the annealed composites were quenched in ice water after being annealed at 200 °C for 8 minutes.

2. Solution Casting Method

Isobe *et al.* [13] prepared a polymer-containing organo-gel by immersing the polymer into a cellulose gel, with the solution being shaken moderately for over five hours. The dry

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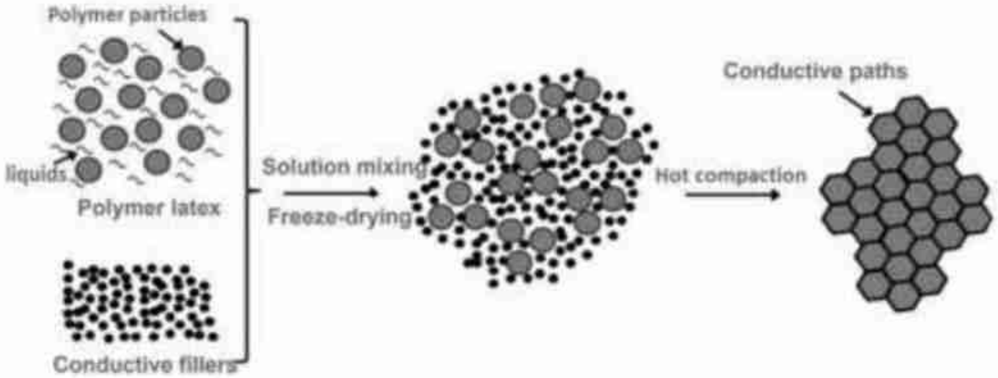

FIGURE 2.3
Fabrication of segregated conductive nanocomposites using the latex technique. Adapted with permission from Reference [8], Copyright (2014), Elsevier.

casting of solutions on glass plates was also used to create pure polymer films. Yin *et al.* [14] prepared functionalized boron nitride nanosheets-1D copper nanowire-poly(vinyl alcohol) [f-BNNS-CuNWs/PVA] film with different concentrations of nanofillers by varying the amounts of functionalized boron nitride nanosheets (f-BNNS) and copper nanowires (CuNWs).

3. Hot-Stretching Process

Song and co-workers prepared a ternary nanocomposite containing poly(vinylidene fluoride) (PVDF) and a fixed $BaTiO_3$ (BT) content of 10%, with a volume percentage of Bi_2S_3 nanorods (fBi_2S_3) ranging from 0% to 120% [15]. Stretched nanocomposite films were then cut into pieces of 10×10 mm. The unstretched films of the nanocomposite were then cut into small pieces and stacked in the hot-press mold for random composites.

4. Melt Compounding

Melt compounding is a method of producing a polymer nanocomposite by combining nanofiller and a polymer melt. This process requires a high temperature under solvent-free conditions.

5. Method of In-Situ Polymerization

In-situ polymerization for the preparation of nanocomposites involves mixing nanofillers directly with monomer solutions and dispersing them as the polymerization takes place, shortening the time it takes to fabricate polymer nanocomposites.

6. In-Situ Polymer Composite Synthesis

The Roy group employed an *in-situ* PNC synthesis approach [16]. For this, Al^{2+}: Nd_2O_3 nanowires were added to an aniline hydrochloride solution in varying proportions by weight (5, 10, 15, 20, and 25 wt%). Then, at a temperature of 0 to 5 °C, 0.25 M ammonium persulphate was gently added to the mixture with steady stirring, and it was left to react

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for 12 hours, yielding a greenish-black precipitate. Structural and morphological characterizations and electrical measurements of the nanocomposites were carried out.

7. Template-Based Method

In this method, oxidation of pyrrole (to polypyrrole, PPy) was carried out with $FeCl_3$/methyl orange, using a template-based technique to produce PPy-based nanocomposites. Using a digital caliper, the polymer film thickness was measured to be roughly 150–170 mm. In recent work, the authors employed atomic force microscopy to explore the surface topography of polymer films. The mean surface roughness of the polymer sheets was discovered to be 250 nm, which would represent a simple sensor component [17].

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8. Sonication

Polypropylene fumarate (PPF) nanocomposites with a 0.2 wt% loading of boron nitride nanotubes (BNNTs) and boron nitride nanoplatelets (BNNPs) were produced *via* sonication. After the addition of the nanomaterial dispersions to a 1:1 mixture of PPF/N-vinyl pyrrolidone (NVP) crosslinker, the preparation was sonicated for 15 minutes. Finally, cylindrical specimens were fabricated by pouring the nanocomposite mixture into Teflon molds and curing overnight at 60 [18].

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9. Radical Polymerization

By altering the quantity of the crosslinking agent or *N*-isopropyl acrylamide (NIPAM), Ma *et al.* [19] produced thermochromic 1D photonic crystal films *via* radical polymerization and an external magnetic field. The samples were then stored in water at ambient temperature for later use.

10. Melt Intercalation Method

Daniel *et al.* [20] used a volumetric-type feeder, the Cloisite-30B (C30B) (1, 2, 3, 5 wt%), PP granules, and Elvaloy-AC3427 (EA), and processed them in a 40:1 length-to-diameter (L/D) ratio with an intermeshing twin-screw extruder. A pelletizer was used to pelletize the water- and air-cooled PP/C30B/EA nanocomposite.

3. Properties of One-Dimensional-Polymeric Nanocomposites

1D-polymeric nanocomposites have many properties, such as crystallization, mechanical, dielectric, antibacterial, thermal, flammability, biocompatibility, resistance-switching capability, and optical properties based on their composition. Some of these valuable properties are discussed below.

1. Crystallization Properties

Some 1D-polymeric nanocomposites show crystallization properties. Hao *et al.* [21] synthesized a 1D-polymeric nanocomposite which is used to enhance the crystallization

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property of the polymer. They looked at the components of the crystallization cycle of polymers grafted onto 1D nanorods, as well as the impact of polymer nanorod cooperation and grafting density on comparison of crystallization results from dynamic Monte Carlo simulations. With the increase in the grafting density, some other parameters increase, such as the number of crystallites, segment density close to the interfacial areas, and the mean square radius of gyration ($\langle R_g^2 \rangle$), which are helpful in the improvement of crystallizability. Idumah *et al.* [22] reported that halloysite nanotubes (HNTs) are another 1D naturally occurring nanomaterial showing a very unique collection of high-aspect-ratio, tube-like structures, normally accessible, with decent biocompatibility, extraordinary functionality, and generally more noteworthy mechanical performance, greater thermal stability, and simplicity of accessibility. Nanocomposites loaded up with HNTs display greatly improved tensile/ductile, toughness and elastic moduli, and flexural strength. Changes in the crystallization behavior of the polymer generated by the integration of HNTs are linked to the primary constituents of HNTs and interfacial interactions in nanocomposites. Therefore, HNT-polymer nanocomposites (HNT-PNCs) have developed a new crystallization property. HNT-PNCs exhibited excellent medication-exemplifying and delivering affinities because of their cylindrical biocompatibility and microstructure, making them ideal for use as medication delivery agents and scaffolding for tissue engineering. The various HNT preparation methods are depicted in Figure 2.4.

2.3.2 Dielectric/Electrical/Piezoresistive Properties

Some 1D-polymeric nanocomposites exhibit dielectric/electrical/piezoresistive properties based on their composition or polymer matrix. The dielectric properties of PNCs have become important because they express the potential for dissipation/energy storage when subjected to an electric field. Pierini *et al.* [23] prepared 1D-conducting PNCs to check their electrical properties by using electrospinning methods. They synthesized nanofibers based on geometric chrysotile nanotubes and polyaniline/poly(ethylene oxide)-doped blends. Electrospun fibers are generally produced from pristine polymers with identical blend-loaded materials mixed with the carbon nanotubes that are also utilized as the reference materials to investigate the electrical and structural properties of such materials. The expansion of materials with greater conductivity altered the electrical characteristics of the materials for the most part. These electrospun fibers that are fabricated with a conventional cover like chrysotile tend to show greater electrical conduction than do the pristine materials. Khurram *et al.* [24] demonstrated the correlation of the dielectric response of the nanocomposites in the microwave range. Avilés *et al.* [25] investigated the piezoresistive responses, electrical conductivity, and mechanical properties of 1D-, 2D-, and 3D-CNT/polymer composites, thermally reduced graphene oxide (FLG), and cubic-shaped few-layer graphene shells (CGSs). Composites incorporating a 1D/2D hybrid mix of CNTs and FLGs or CNTs alone have greater piezoresistive sensitivity. The increased piezoresistive sensitivity of the material is attributed to their higher excluded volume. Chu *et al.* [26] demonstrated that the larger aspect ratio led to improved dielectric properties of polymer nanocomposites. 1D nanofibers (TiO_2/C nanofibers, NFs) are practical examples of it. Chu *et al.* also synthesized a TiO_2/CNFs /poly(vinylidene fluoride-hexafluoropropylene) (TiO_2/CNFs/P(VDF-HFP)) nanocomposite to improve dielectric properties.

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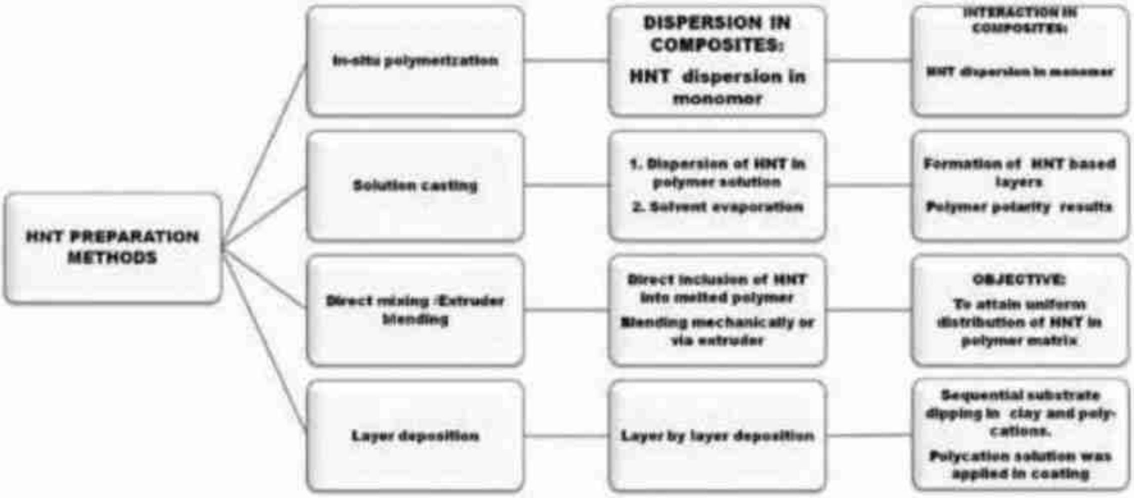

FIGURE 2.4
Preparation methods of HNT-polymer composites. Adapted with permission from Reference [22], Copyright (2019), Taylor & Francis.

3. Mechanical Properties

Traditional metals have been extensively replaced by PNCs mainly because of the latter's unique properties in various engineering applications. The enhanced mechanical properties, like increased wear/fatigue resistance, also allow the use of these materials in military and aerospace applications [27]. Pradhan *et al.* [28] investigated the effect of filler dimensionality on the mechanical properties and morphology of the nanocomposites by utilizing different kinds of nanofillers like layered silicate (2D filler), multi-walled carbon nanotubes (1D filler), and boehmite (3D filler). The nanofillers were first dispersed in the matrix of a polyolefin-based elastomer known as ethylene-1-octene copolymer (EOC). Based on the results of the microhardness measurements and tensile tests of the samples, it appeared that the nanofiller's reinforcing action occurred in the following order: 1D filler > 2D filler > 3D filler. Avilés *et al.* [25] reported that the findings of the preceding experiments showed that composites containing a 1D-2D hybrid blend of CNTs and FLGs or CNTs alone had better mechanical properties. This improved performance can be attributed to the greater aspect ratio/lateral size, functionalities, more dangling bonds, and greater specific surface area in the case of FLGs as nanofillers, as shown by the above experiment.

4. Antibacterial Properties

Silver nanoparticles show excellent antibacterial properties. Zhang *et al.* [29] reported that 1D PNCs show antibacterial properties. They prepared novel β-cyclodextrin/poly(*N*-vinylpyrrolidone) (β-CD/PVP) composite nanofibers having silver nanoparticles generated by the electrospinning technique for the antibacterial study, using *Staphylococcus aureus* and *Escherichia coli* as model species.

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5. Thermal Stability

PNCs are hybrid materials, consisting of a dispersed inorganic filler, with at least one nanometer-scale dimension, in an organic polymer matrix. Adding a small amount of nanofiller changes the polymer's macroscopic characteristics dramatically. In addition, the fillers have a relatively high aspect ratio. In comparison to plain polymer materials, nanocomposites offer much improved features, such as improved heat stability and mechanical characteristics. HNTs have a wide range of possible uses in PNCs, owing to their superior heat stability. HNTs are naturally occurring 1D nanomaterials made up of mainly hollow tubular nanostructures with high aspect ratios. As a result, they have excellent mechanical strength, biocompatibility, thermal stability, and availability. The HNT-PNCs show improved potential for the design and growth of high-performance compounds for environmental safety, biomaterials, and the aircraft/automobile industries. These materials have been utilized to thermally stabilize polyamide-6 (PA6), polypropylene (PP), linear low-density polyethylene (LLDPE), polyethylene terephthalate (PET), and polybutylene terephthalate (PBT). These materials are used as environmentally friendly inclusions in polymer materials due to their inherent barrier effect against mass movement and heat at the time of the nanocomposite's combustion. When iron was added to HNTs, the thermal stability of the nanocomposites improved further.

6. Fire Retardance/Flammability

Based on the intended thermal application of the materials, the addition of the nanofillers can be designed for one of two purposes, namely increased thermal conductivity or reduced flammability. The heat release rate, which is a critical factor in assessing a product's flammability and fire hazard, can be used to determine the flammability of any material. In recent years, the scientific community has shown a strong interest in polymeric materials with unique qualities such as fire resistance, greater mechanical strength, and largely decreased or increased temperatures. Problems caused by fires include pollution of the environment by the production of large volumes of smoke, combustion products, and thermal decomposition, while the excessive heat that is produced during the results in significant material losses. Combining polymers with a variety of fire retarding agents to generate composites with particular component characteristics can significantly increase polymer fire resistance. HNTs can be used as a very efficient fire retardant material for incorporation into polymers because of their tubular structure and thermal stability. Due to their surface acidity, HNTs can also be catalyzed, resulting in a very protective polymeric coat-like char that decreases the heat release rate (HRR). Passive fire protection materials (PFP) have been closely examined quantitatively through constant heat-flux propane-burner tests, with PFPs fabricated on a steel substrate. The findings of the burner tests show that the materials can produce a large, continuous heat flux, similar to what is seen in a strong fire. Furthermore, the results demonstrate that the HNT materials included created exceptional fire resistance, in contrast to other nano-materials that only showed a minor improvement. Dumazert *et al*. [30] studied the poly (1, 4-butanediol succinate) (PBS) nanocomposites, having two halloysite and sepiolite materials to investigate and demonstrate its thermal stability and fire retardancy properties *via* thermogravimetric analysis (TGA). Zhang *et al*. [31] also developed a novel hybrid (GHNT) comprising of HNTs and graphene oxide (GO), as well as composites based on cyanate ester (CE) resin. The effects of GHNT on fire retardancy, smoke suppression, and heat resistance in GHNT/CE composites were examined.

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7. Biocompatibility

Biocompatibility is another important property of 1D PNCs. Farshid *et al.* [32] synthesized PNCs by utilizing decomposable polymers such as poly(propylene fumarate), *N*-vinyl pyrrolidone (NVP) as the crosslinking agent, and a nanomaterial (such as SWCNT/MWCNT, graphene oxide nanoplatelets, tungsten disulfide nanotubes, or molybdenum disulfide nanoplatelets). The authors also demonstrated *in-vitro* cytocompatibility of such nanocomposites (Figure 2.5).

Armentano *et al.* [33] investigated the biocompatibility of HNTs. This property helps HNTs to gain the position as an essential nanomaterial for increasing numbers of biomedical applications. Recently, HNT-PNCs are practically utilized in drug delivery, tissue engineering, bone implants, cancer therapy, and cosmetics. HNT-based materials have also been fabricated into biodegradable polymers materials, like polylactide (PLA), polyvinyl alcohol (PVA), chitosan, and poly(lactic-co-glycolic) acid (PLGA) for the synthesis and design of scaffolds for tissue engineering.

8. Resistance-Switching Capability/Mechanoresponsiveness

The option for flash memory or other dynamic random-access memory (DRAM), such as magnetoresistive RAM (MRAM), resistance-switching RAM (RRAM), ferroelectric RAM (FeRAM), and phase-change RAM (PCRAM), has been recommended. RRAM based on metal–insulator–metal (MIM) structures has recently been thoroughly investigated as one of the most promising next-generation memory candidates due to its low power consumption, non-volatility, high operation speed, similarity to conventional Si-based process, and simple structure. Jeon *et al.* [34] prepared 1D conductive nanomaterials, such as CNF or CNT coated with TiO_2. In repeated switching investigations, the carbon nanotube-TiO_2

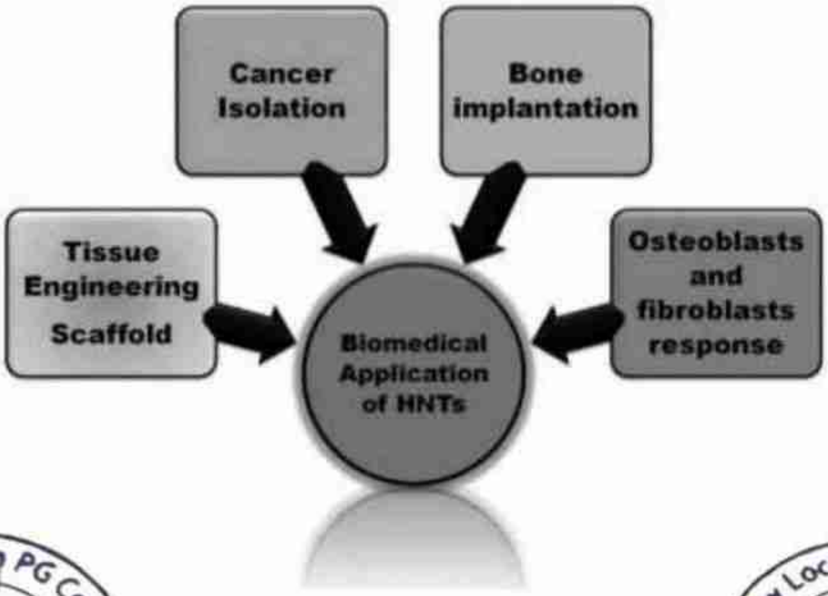

FIGURE 2.5
Various biomedical uses of HNT-PNCs. Adapted with permission from Reference [22], Copyright (2019), Taylor & Francis.

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and CNF-TiO$_2$ mixed composites show a constant resistance-switching action with a high on/off ratio, as well as increased switching stability.

2.3.9 Optical Properties

Photonic crystals (PCs) have two components in a periodic array with different refractive indices, such as colloidal crystalline arrays (CCA) and Bragg stacks. In comparison with other photonic crystals (PCs), the responsive photonic crystals are generally able to make a change in the refractive index contrast or periodic lattice spacing. Therefore, they can modulate the color induced by different stimuli like magnetic fields, ionic concentrations, electric fields, pH, temperature, and stress. As a result, responsive photonic crystals are a prospective choice for structural displays and color printing, bioassays, optical devices, outdoor signage, and sensors, and anti-counterfeiting devices, among other applications. Ma *et al*. [19] demonstrated the optical properties of 1D polymer nanocomposite materials. They used a sterically stabilized magnetically responsive photonic crystal (MRPC) for producing flexible thermochromic films on a centimeter scale.

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4. Application of One-Dimensional Polymeric Nanocomposites

1. Nanofiller Release

Polymer nanocomposites (PNCs) are used for various commercial purposes, such as food packaging, building infrastructure, biomedical devices, and implants. Duncan *et al*. [35] explained that the nanofiller (such as engineered nanomaterials (ENMs)) could be released from the PNCs into the liquid medium. that there are four possible mechanisms (desorption, dissolution, diffusion, and degradation of the matrix) to release the ENM from PNC materials (Figure 2.6).

2. Energy Storage Capacitor

The design and development of compact, affordable, and super-functioning electric energy storage devices have been challenging for researchers around the world. The polymer-based nanocomposite film capacitors are generally considered to be superior to other materials because of their high-speed charging/discharging, high power density, long cycle life, and high operation voltage for energy storage devices. The Pan group [37] prepared 1D lead-free $0.5(Ba_{0.7}Ca_{0.3})TiO_3$–$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ nanofibers (BCZT NFs) through the electrospinning method. The same research group [38] subsequently reported the synthesis of artificial PNCs, using a new hybrid structure that includes 1D Ag@BaTiO$_3$@polydopamine@Ag nanofibers (1D ABPAs NFs) as fillers and P(VDF-HFP) as a matrix. The material developed demonstrated remarkable inclusive performance. Lin *et al*. [39] looked into sandwich structure ceramic/polymer composites, using 1D PVDF/K0.5Na0.5NbO3 nanofibers composites as the intermediate layer and PVDF as the outer layer for energy storage applications.

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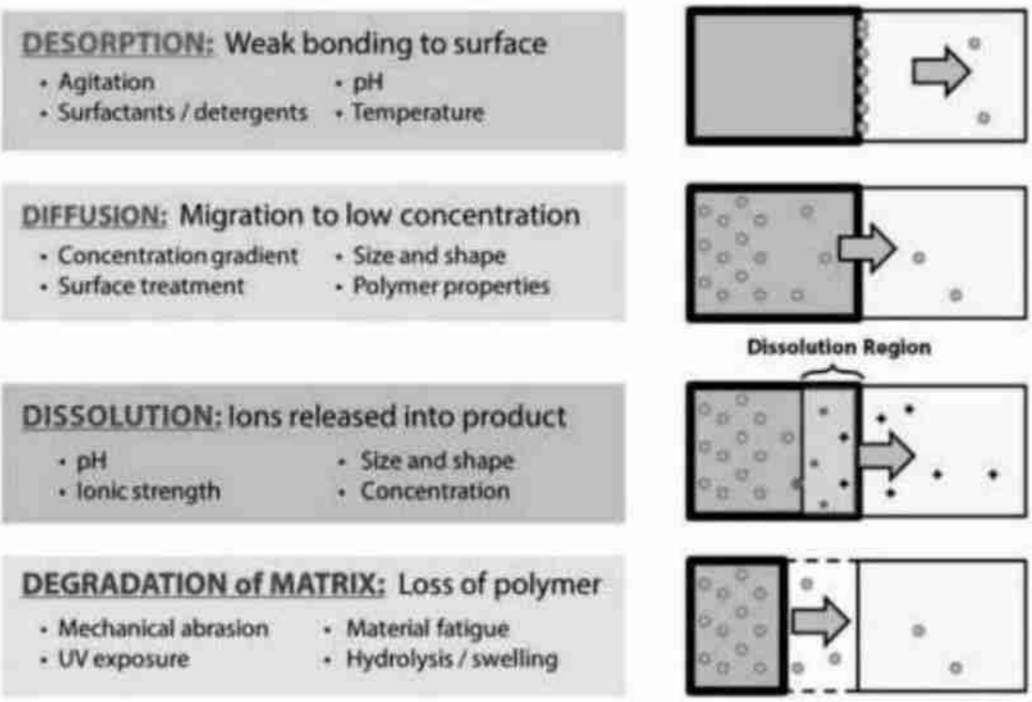

FIGURE 2.6
Schematic diagram of four possible mechanisms of ENM release from PNC materials. Adapted with permission from Reference [36], Copyright (2014), Wiley.

3. Electro-Optic (EO) Modulator

Inou *et al*. [40] designed and tested an electro-optic (EO) modulator made up of 1D photonic crystal nanobeam waveguides, composed of polymer/silicon hybrids. Results revealed that the EO polymer/silicon hybrid photonic crystal nanobeam waveguides produce an efficient and superior platform.

4. Lithium-Ion Solid-State Batteries

The solid-state lithium-ion batteries (LIBs) have evolved in recent years as an alternative energy supply for vehicles because of the limited supply of fossil fuels and because of the environmental issues raised and the requirement for a low-carbon economy in today's world. One of the major components of electric vehicles is rechargeable LIBs. The effect of adding various 1D $NiCoO_2$ nanosheets (NSs)@amorphous CNT composites was investigated by Xu *et al*. [41], who discovered that the composites had a long cycle life. Sulfonated PNTs were also able to stretch out to develop a variety of other useful 1D metal oxides@ amorphous CNT nanostructures. Zhu *et al*.[42] synthesized a polyethylene oxide (PEO)-based polyelectrolyte, loaded with 1D ceramic $Li_{0.33}La_{0.557}TiO_3$ (LLTO) nanofibers.

5. Biomedical/Bone Tissue Engineering

Shi *et al*. [43] reported the use of SWCNT/eco-friendly PNCs in application to bone tissue engineering based on 1D and 2D boron nitride nanomaterials. Farshid *et al*. [44] studied the *in-vitro* cytotoxicity and the mechanical properties of the materials. The scaffolds for

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tissue engineering are generally made up of the synthetically/naturally occurring substances used for shaping the growth of cells.

6. Strain-Sensing Behaviors

A flexible strain sensor was created by combining graphene woven fabrics and polydimethylsiloxane (PDMS). This wearable sensor can also identify human beings in action, which also include expression change, pulse, hand clenching, phonation, blinking, and breathing. Li *et al.* [45] developed a wearable wrist bracelet composed of a carbon sponge (CS)/PDMS composite. Chen *et al*. [46] demonstrated the effect of filler dimensionality on the strain-sensing behavior of isoprene rubber (IR)-constructed conductive composites on the surface of a computer.

7. CO_2 Solubility and Diffusivity

Several investigations reported swelling of polymer/CO_2 systems and changes in the CO_2 diffusion coefficient in various pure polymers. Hu *et al*. [47] studied the effects of polymer aggregation states (melt and solid phases) and layered filler-containing 1D nanostructures on CO_2 diffusivity and solubility (nano-MMT).

8. Thermoelectric Composites

Design and the development of flexible advanced thermoelectrics depend upon the mechanical flexibility and superior thermoelectric (TE) performance, and the sustainability of essential elements. Xu *et al* [48] studied a flexible thermoelectric composed of PVDF/Ta_4SiTe_4 organic-inorganic composites. The authors demonstrated a proof-of-concept investigation with flexible thermoelectric modules, explaining the efficacy of the dimensionality/morphology-matching technique.

9. Flexible Piezoresistive Tactile Sensor/Sensors and Actuators

The different industrial processes in the agriculture field, including fertilizer production, and the food technology industry, require the sensitive and accurate detection of ammonia due to the toxicity of ammonia gas. In addition, increased inhalation of ammonia may lead to many harmful, clinical conditions. The ammonia gas-sensing action of 1D polypyrrole-metal oxide nanocomposites was demonstrated by Joulazadeh *et. al.* [49], using zinc oxide (ZnO) or tin dioxide (SnO_2) nanoparticles/polypyrrole (PPy) nanocomposites.

10. Tensioning Cables

Recently, researchers have focused on the use of 1D polymeric nanocomposites in the tensioning cable application, along with various other applications as discussed above. CNT strands have a larger surface area than carbon fiber due to their small size, which may allow for more developed load transfer between the polymer and the filler. The mechanical parameters of the CNT/bismaleimide (BMI) composite fiber were the most notable, with modulus and tensile strength of 232–315 GPa and 4.5–6.94 GPa, respectively. CNT/epoxy nanocomposites have been employed in high-tension applications, including pressure vessels (COPVs), which are used to keep a spacecraft's cryogenic tank at a consistent pressure.

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11. Shielding against Electromagnetic Interference

Electromagnetic interference (EMI) shielding can affect the signal/response of electrical devices and is also harmful to human health. As a result, EMI should be protected against electromagnetic radiation. In recent years, shielding devices have decreased in size, and shielding with a thin- profile and low-weight device has become popular. To scatter, reflect, or absorb electromagnetic radiation, the EMI shielding materials must be conductive and/or magnetic. Metal, on the other hand, has quite high effectiveness in terms of electromagnetic interference shielding (EMI SE). The polymer-based nanocomposite materials tend to attract more attention as they show desirable properties such as being lightweight and non-susceptible to corrosion, with high processability.

12. Thermal Barriers

Nanofillers are mainly used to reduce the flammability of material and to enhance its thermal conductivity. Heat discharge rate is an extremely significant characteristic for determining a material's flammability and fire hazard; the higher the value, the faster the heat transfers across a material. The nacre-inspired ceramic-based nanosheet materials can be considered for thermal barrier applications as they have extremely high thermal resistance and are a very favorable candidate for thermal barrier applications. Several nacre composite materials utilize flammable polymers like polyacrylic acid or polyvinyl alcohol. The nacre-based materials' flame resistance can be encouraged by selecting a fire-resistant polymer, such as the micron-thick montmorillonite/polyanion composite, which has much higher flame retardancy than montmorillonite (MTM)/polyvinyl alcohol.

2.5 Summary and Perspectives

In conclusion, one-dimensional polymeric nanocomposite materials, such as carbon nanotubes, graphene, and fullerene, provide a unique chance to combine the features of polymers and nanocomposite materials. These combinations open up new possibilities for engineering, high-tech enterprises, and medicinal applications. However, the successful formation of polymeric nanocomposites for industrial application with suitable viscosity, thermal, and conductive properties will require more research on the polymerization protocols/processes. Once accomplished, this will lead to ~~a major shift in the potential~~ applications of such materials in everyday life. Several str[illegible] been developed to produce polymer nanocomposites from a solution-casting method, hot stretching process, sonication, melt intercalation, and electrospinning technique. In this chapter, we have looked at the engineering and biomedical properties of various one-dimensional polymer nanocomposites to explore their potential applications.

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“असंगठित क्षेत्र में काम करने वाले श्रमिकों की आय और रोजगार का एक विश्लेषणात्मक अध्ययन”

(छत्तीसगढ़ राज्य में बिलासपुर जिले के बिलासपुर शहरी क्षेत्र के संदर्भ में)

राजेश कुमार बघेल*

सारांश

शोध पत्र असंगठित क्षेत्र से संबधित विभिन्न आयामों को समझने की एक पहल है। अधिकांश श्रमिको का उल्लेख है कि अकुशल श्रमिक मुख्य रुप से भारत में असंगठित क्षेत्र में खुद को संलग्न करते है। शोध पत्र का उद्देश्य असंगठित क्षेत्र के श्रमिकों से संबधित विभिन्न मुद्दों को जानना है। प्रस्तुत अध्ययन के लिए प्राथमिक आँकड़ो का प्रयोग किया गया है। असंगठित क्षेत्र अर्थव्यवस्था के विकास में महत्पूर्ण भूमिका निभाता है। श्रमिकों को कुछ मुख्य समस्याओं का सामना करना पड़ा जैसे–कम मजदूरी दर, कम आय और बचत, खराब शिक्षा और स्वास्थ्य की स्थिति, कठिन कामकाजी जीवन, उत्पीड़न, अपर्याप्त और असमान मजदूरी संरचना, लंबे समय तक काम करने के घंटे, खराब आवास सुविधाएं, सुरक्षा उपायो की कमी और उचित शिक्षा के लिए निर्माण श्रमिकों के बच्चों, रोजगार और प्रौद्योगिकी की कमी, बाजार अभिविन्यास और गरीबी अधिक है और कोई सामजिक सुरक्षा नहीं है, श्रमिकों को लाभ प्रदान किया जाता है।

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* सहायक लिपिक

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असंगठित क्षेत्र के श्रमिकों में कुल मिलाकर आर्थिक–सामाजिक स्थितियाँ बहुत कमजोर है। यह विषय हमारे समाज के लिए बहुत ही चुनौतीपूर्ण है।

भूमिका

भारतीय अर्थव्यवस्था के लिए असंगठित या अनौपचारिक क्षेत्र सबसे महत्वपूर्ण है। लगभग 92 प्रतिशत कार्यबल और लगभग 50 प्रतिशत राष्ट्रीय उत्पाद अनौपचारिक अर्थव्यवस्था के लिए जिम्मेदार है। श्रम शक्ति विभिन्न क्षेत्रों में शामिल है, एक कामकाजी–मजदूरी श्रमिकों, आकस्मिक श्रमिकों, अनुबंध श्रमिकों, अर्थव्यवस्था के असंगठित क्षेत्र में स्वरोजगार के रुप में, लेकिन अर्थव्यवस्था – सामाजिक स्थिति बहुत खराब है और कम मजदूरी आय, कम बचत, कम है क्रय शक्ति और कम बल गरीबी, बेरोजगारी, अशिक्षा का सामना करते हैं और निम्न स्वास्थ्य का भी सामना करते हैं। और श्रम बल बिना किसी लाभ और सामजिक सुरक्षा के अनौपचारिक क्षेत्र में काम कर रहे हैं।

उद्देश्य

- असंगठित क्षेत्र में कार्यरत श्रम बल की सामाजिक–आर्थिक स्थिति का अध्ययन करना।
- असंगठित क्षेत्र में कार्यरत श्रम शक्ति की आय, रोजगार और उपभोग की प्रवृति का अध्ययन करना।
- असंगठित क्षेत्र में कार्यरत श्रम शक्ति के संतुष्टि स्तर का अध्ययन करना।
- असंगठित क्षेत्र में कार्यरत श्रम बल के जीवन स्तर में सुधार के लिए सुझाव देना।
- शोध क्षेत्र की सीमाएं
- यह अध्ययन केवल बिलासपुर शहर के क्षेत्र तक ही सीमित है।
- इसके तहत असंगठित क्षेत्र में कार्यरत श्रम बल की आय, और रोजगार के पैटर्न का अध्ययन किया जा रहा है।

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- यह अध्ययन शोध कार्य के लिए केवल चालू वर्ष यानी 2019–20 तक ही सीमित है।
- शोध कार्य के लिए अनुसंधान तकनीको ंका प्रयोग सीमित है।

शोध परिकल्पना

- विवाहित श्रमिकों और उनके आयु वर्ग के बीच महत्वपूर्ण संबंध है।
- शैक्षिक स्तर और श्रम शक्ति के बीच कोई महत्वपूर्ण संबंध नहीं है।
- असंगठित क्षेत्र में कार्यरत श्रम शक्ति की आय स्तर में वृद्धि हुई है।
- कार्य के उपभोग की प्रवृति में वृद्धि होती है। श्रमिकों के बचत स्तर में वृद्धि हुई है।
- श्रमिकों की ऋण स्थितियों में कोई परिवर्तन नहीं हुआ है।
- काम की प्रकृति के संबंध में श्रमिकों के संतुष्टि स्तर में कोई सुधार नहीं हुआ है।

शोध प्रविधि

यह अध्ययन प्राथमिक आंकड़ों पर आधारित है। बिलासपुर में शहरी क्षेत्र को अलग रखते हुए अप्रैल 2019 से मार्च 2020 तक सर्वेक्षण किया गया है। ऐसा करने के लिए, शोध अध्ययन के लिए आवश्यक जानकारी प्राप्त करने के लिए एक 'अनुसूची' विकसित की गई है। असंगठित क्षेत्र में चयनित कुल 300 श्रमिकों (रिक्शा चालक –100, भवन निर्माण श्रमिक–200, को सुविधा के नमूने और विचार के आधार पर लिया गया है, जिनमें से 38% महिला और 62% पुरुष श्रमिक है।

अध्ययन के उद्देश्य से 13 कार्यस्थलों का चयन किया गया है। उपयुक्त उद्देश्यों को ध्यान में रखते हुए रिक्शा चालकों और भवन निर्माण श्रमिकों के बीच साक्षात्कार आयोजित किया गया है। इस प्रकार एकत्र किए गए डेटा का उपयोग उत्तरदाताओं की आर्थिक–सामाजिक और आय और रोजगार की स्थिति के परिणाम पर पहुंचने के लिए किया गया है। विभिन्न आर्थिक गतिविधियों के प्रभाव का विश्लेषण करने के लिए मात्रात्मक और गुणात्मक दोनों दृष्टिकोणों का उपयोग किया गया है। यह खंड संक्षेप

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में उन चुनौतियों को उठाता है जिनका शोधकर्ताओं को पहचान, मापन, मॉडलिंग और व्याख्या के संदर्भ में सामना करना पड़ता है।

रोजगार के आंकड़ों के लिए सामान्य स्थिति दृष्टिकोण का उपयोग किया गया है क्योंकि इसे रोजगार में मौसमी उतार–चढ़ाव को व्यक्त करने के लिए अर्थव्यवस्था में आर्थिक गतिविधियों का सबसे उपयुक्त उपाय माना जाता है। सरल वर्णनात्मक सांख्यिकीय उपकरण – सारणीकरण, ग्राफ, माध्य, मानक विचलन, मानक त्रुटि, ची–स्क्वायर (X2), Z- टेस्ट का उपयोग उन कारको को सामने लाने के लिए किया गया है जिनका उत्तरदाताओं के बीच रुग्णता पर असर पड़ता है।

शोध साहित्य का पुनरावलोकन

देवी एटल (2015) लेखकों ने विभिन्न संगठनों में काम करने वाले लोगों की कामकाजी परिस्थितियों को आंकने की कोशिश की। वर्तमान वैश्वीकृत कार्य वातावरण के तहत कर्मचारियों को बनाना महत्वपूर्ण है वर्तमान अध्ययन की एक महत्वपूर्ण परीक्षा है। विभिन्न उद्योगों में समान प्रकार के कार्य करने वाले श्रमिकों के बीच पेशी–कांकालीय विकारों पर साहित्य में चयनित मामले मौजूद है, और इस सवाल का जवाब देते है कि क्या इन उद्योगों में लगे श्रमिकों के बीच पेशी विकारों के प्रकार और स्तर समान है या नही।

कल्याणी (2015) ने इस लेख में असंगठित श्रमिकों की स्थिति का विश्लेषण किया है, जिसमें आम तौर पर भारतीय श्रम शक्ति की मुख्य ताकत माना जाता है। राष्ट्रीय नमूना सर्वेक्षण संगठन (एनएसएसओ) द्वारा 2009–10 में किए गए एक सर्वेक्षण के अनुसार, देश में कुल रोजगार 46.5 करोड़ है, जिसमें संगठित क्षेत्र में लगभग 2.8 करोड़ और असंगिठत क्षेत्र में शेष 43.7 करोड़ कर्मचारी शामिल है। यह पहचाना गया है कि आजकल भारत में अधिकांश अनौपचारिक रोजगार श्रम बाजार परिदृश्य की केन्द्रीय विशेषताओं में से एक रहा है। जबकि यह क्षेत्र देश के सकल घरेलू उत्पाद में लगभग आधा योगदान देता है, रोजगार के मोर्चे पर इसका वचन ऐसा है कि कुल कार्यबल का 90%

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से अधिक अनौपचारिक अर्थव्यवस्था में लगा हुआ है। यह व्यापक रुप से स्वीकार किया जाता है कि भारत में अनौपचारिक क्षेत्र, औपचारिक क्षेत्र की तुलना में कम उत्पादकता विकार से ग्रस्त है। लेखक ने खाद्य, पोषण, स्वास्थ्य, आवास, रोजगार, आय, जीवन और दुर्घटना, और वृद्धावस्था जैसे असंगठित क्षेत्र की सुरक्षा आवश्यकताओं में सुधार करके सुझाव दिया है। अभी भी असंगठित क्षेत्र की उद्घोषणा सरकारों के साथ अप्राप्य है।

कपूरेताल (2014) इस पत्र में शोधकर्ता असंगठित क्षेत्र में श्रमिकों के काम करने और रहने की स्थिति को समझने का प्रयास करता है और संगठित और असंगठित क्षेत्र के बीच अंतराल की पहचान करने का प्रयास करता है। असंगिठत क्षेत्रों को मौसमी रोजगार और संविदात्मक कार्य की स्थिति की विशेषता है। कोई सामाजिक सुरक्षा और कल्याणकारी कानून नहीं है। इस क्षेत्र में लोगों को खराब स्वास्थ्य स्थितियों, घटिया कामकाजी जीवन और काम पर उत्पीड़न, अपर्याप्त और असमान वेतन संरचना, लंबे काम के घंटे, खराब आवास सुविधाएं , सुरक्षा उपायों की कमी, और श्रमिकों के बच्चों के लिए उचित शिक्षा की कमी जैसी समस्याओं का सामना करना पड़ता है। इस क्षेत्र में श्रमिकों की स्थिति में सुधार के लिए सरकार को हस्तक्षेप करना चाहिए और आवश्यक कारवाई करनी चाहिए।

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10. Indian Fnglish Writers

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Introduction

Indian English literature is also known as Indian English Writing. It consists of the writers who belong to India and write in English language but their native and co native could be in India or abroad their language can be anything in the numerous languages in the country. In this regard there are many diasporic writers who don't live here but continue to write in English. Indian English writing started in the late 1800s with the writers like Henry Louis Vivian Derizio and Michael Madhusudan Dutt followed by the literature genius Shri Rabindranath Tagore and Shri Aurobindo. In the later 1930s writers like Mulk Raj Anand R.K Narayan and Raja Rao have successfully contributed to the growth and popularity of English writing.

Indian philosophy is the system of thinking and thought that was reflected in the civilization of the Indian society. It includes both the systems i.e., the astika system which is an orthodox method way of thinking like Nyaya, Samkhya yoga etc and nastika system which is an unorthodox way of thinking like Jainism, Buddhism etc. Indian philosophy has been concerned with various philosophical problems which are the matters of the world and also contains the mysteries of universe like the nature of the world (cosmology), the nature of reality

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(metaphysics) logic ethics etc. Indian philosophers are respected not only in India but with the whole world their writings and teachings are celebrated everywhere. Some of the philosophers like Buddha, Adi Shankara Naga Arjuna are some of the selebrated philosophers.

Indian English writers and philosophers have contributed a lot to the world in their form of writing and philosophy Adi Shankara or Known as Shankaracharya is Lown as the father of the Indian Philosophy. Indian philosophy is not only concentrated to the matters of society but is also expanded to the universe and its findings.

Contribution of Indian English Writers to the World

The language ‘English’ came to India with the British and the contribution to promote its writing also goes to them. English has been the language of the elites in the Ldian society. It not only influenced our society but also the minds of the Indian society. It also helped in the deconstruction of the Indian nationalist movement. In the last two centuries Indian writing has drastically changed itself and improvised with great maturity. Indian writers have gained a immense confidence to express their emotion in English and contribute their pañ in the world literature.

English writing has been in use for more than two centuries. The first English book was written in 1794 by Sake Dean Mohammad named ‘rfie *tYOVPfS Op Dean Mohammad’.* In the early years Indian writings were

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majorly influenced by the westen thinking. Writers used unadulterated Indian words to show Indian emotion and present an experience which is Indian. In the early times writings were concentrated to few minds and few ideas but the scenario has drastically been changed in the contemporary world. Indian novels have a variety of ideas and thoughts to offer the world. It has shown a great variety and maturity in all the spheres of the English language.

There are many countries in the world that produces their work in English and India is one of them. India has been the third largest producer of the English works in the world. Hundreds of Indian writers have been produsing their works in English and many of them have achieved a global success. Shri Rabindranath Tagore was the first Indian to win a Nobel prize in literature in 1913. He used to write in both Bengali and English and was responsible for the translations of his works his works influenced many great writers like W.B Yeats who did the translation of his award-winning work Geetanjali'. Along with him there are many other writers who have contributed significantly in the world literature.

Indian Writers in the Early Pre-Independence Era

Indian writing is been two centuries old. English was seen as a language of the upper-class society. English was added in our society and culture after the invasion of the British and they stañed colonizing it. Firstly, the language was used for the purpose of trade and commerce and after that it was used in the other purposes like speeches, writing and

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letters. English been a great source of communication to express your thoughts and emotions as it serves as a global language. It became easy to send your thoughts to the world. Because of the language we had great orators like Swami Vivekanand, Bal Gangadhar Tilak and Srinivasa sastri. The few Indian writers have been discussed below -

Gurudev Rabindranath Tagore-

He was a South Asian Bengali polymath who was a great writer, philosopher, social reformer, music composer and painter. He has largely contributed in reshaping the Indian art and music in the late 19 and 20^ century his works has greatly inhuenced the world in transiting the Bengali literaYre. He was the founder of the "profoundly sensitive fresh and beautiful" poeŁy 'Geetanjali'. He was the first non-European to win the prestigious award Nobel prize in 1913 for his work Geetanjali. He was a member of the Hoyal Asiatic Society and was often refened as the "Bard of Bengal".

Rabindranath Tagore was greatly known for his poetry, he also wrote songs essays, short stories, travelogues, dramas and lot of songs. Out of Tagore's prose works his short stories was highly regarded. He was also credited in writing auto biographies his travelogue *Europe jatrir Patro {letters from Europe)* and *Manusher Dharmo* has been compiled into several volumes. He wrote more than 150 works that include poetry songs etc. He was credited in creating several genres in dramas, prose, songs. His songs are also Lown as *Rabindra Sangeet.* India's National añ gallery contains more than 102 works of Tagore

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Michael Madhusudan Dutt (1824-1873)-

Another great writer of that age is Michael Madhusudan Dutt was a great Bengali poet and playwright. He was born in Sagardari a village in keshabpur, Upazila , Jessore district in Bengal. He belonged to a upper middle class elite hindu family. His father Rajnarayan Dutt worked as a special pleader in the sardar Diwani adalat and his mother Jahanvi Devi was a devoted house wife. Dutt was highly appreciated by his teachers and they treated him as a precocious child and treated him as a highly gifted child. His parents were highly well-off family and for that reason he received well education from his family. He studied in an English medium school and not only that he received additional tutorship for English at home. His father's intention behind his western education was to open the doors for the government job for his son.

Madhusudan Dutt wrote extensively in English in his early years. His work *The Captive Ladie* was published in 1849 and it was a long narrative poem like Derozio's, In the *Anglo Saxon and the Hindu (1854)* the quotations and references influenced from the works of William Wordsworth and John Milton. He was bohemian and Romantic by spirit. not only wrote in English but also in his native language Bengali. During his Calcutta years he wrote 5 Bengali plays *Sermista, padmavati, Ekei ki bole sabhyata, Krishna Kumari and buro saliker ghore Ron.* His most celebrated work Meghnad Bodh Kavya was published in 1871 followed by Tilottama Sambhava Kavya and Brajagana Kavya and Veerangana kavya. He translated

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many plays from Bangla to English including his play Sermista.

Sarojini Naidu (1879-1949)-

Sarojini Naidu was an Indian political activist and poet. A proponent of civil rights, women empowerment and anti-imperialistic ideas she was an important figure in the India's stnggle for the Independence. She was also a prominent figure in the Indian English writing and dueto her colour and lyrical kind of poetry she earned the title of “Nightingale of India” or “Bharat Kokila” by none other than Mahatma Gandhi. Her poetry includes poetry for both adults and children. Her poetic themes include serious matter like patriotism and tragedy. “In the Bazaars of Hyderabad” remains one of her popular poems.

Naidu started writing at a very young age at 12. Her poem Yofior *Mvnner* wütten in Persian was highly impressed by the Nizam of Hyderabad. Naidu's poetry was written in English and she uses the form of lyric poetry in the era of British Romanticism which she tried to reconcile with her Indian Nationalist political thoughts. She was Lown for her wide use of sensory images and her depiction of lush India. Because of her lyrical nature she was also known as the “Indian Yeats”. Her other works include The golden threshold, the bird of the time songs of life, death and the spring etc.

The other Indian writers of the Indian English Writing includes Henry Dorezio, Bankim Chandra Chattopadhya,

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Arbindo Ghosh, Nirad C. Chowdhary, Toru Dutt, R.K Narayan, Raja Rao, MulLaj Anand etc.

Indian Writers in the Post Independence Period

Indian writing had a drastic shift in its form from the pre independence period to the post-independence period more genres were added from black and white canvas to multi colored background to attract more readers and audience this new shift made the reading more attractive and appealing. Poetry had been a popular method of expression during this period poets like Sarojini Naidu and Kabir were popular this time. Literature at this time saw some great changes in the form of creative writing and literary writing. Post-independence works saw many more richer languages and literatures beyond the limited scope of their own personal culture and mother tongue. Yany translation works were encouraged during this period. Post-independence literature showed a creative and permanent literature that blooms out the tragedy of the past.

R. K Narayan (1906-2001)-

Rasipuram Krishnaswami Iyer Narayanswami was a dynamic author of the post-independence period. He was an Indian writer who was known for his skill set in the fictional town of Malgudi. He was a leading author in the Indian English writing who did a tremendous job both in the children and adult reading other authors in his period include Mulk Raj Anand and Raja Rao.

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The writing style of Narayan was quite natural and humorous. He focused mostly on making ordinary people his making his main characters people from his neighborhood cousins and family members provide a relatable character that would attract his audience. He gave new heights to the fictional characters. He was known as the Indian Chekov due to the similarities in his writing. Out of the main works include The guide, the man eater of Nfalgudi , waiting for the Mahatma etc. he has written a number of short stories and prose version of the two epics The Ramayana and The Mahabharata.

Mulk Raj Anand (1905-2004)

Like R.K Narayan Mulk Raj Anand was another important personality in Indian Writing. He was greatly depicted his life to the lives the poor classes in the Ldian society. He was one of the pioneers of the Indo Anglican society together with R.K Narayan and Raja Rao and he was one of the writers in India who achieved international acclaim. He was greatly known for his shoa stories and works which is a good example of modern Indian English Literature and his writings were dedicated to the lower class, Oppressed by the society.

He was best known for his work Untouchable followed by the other works called coolie which was also depicted in a movie and Two leaves and a bud. He was also the first writer to incorporate Hindi and Punjabi idioms in the English language and was also awarded the third highest civilian award of India Padma Vibhushan.

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Raja Rao (1908-2006)

Raja Rao was an Indian American writer who wrote in English language whose interest was mainly inveHed towards metaphysics. He was the eldest of all his nine siblings his father was a teacher in kannada language in the nizam college of Hyderabad and his mother was a home maker. His mother died when Raja Rao was a 4-year-old kid. His mother's death left a deep impact in the child's mind and the orphan hood was clearly seen in many of his works another great influence of Raja's life was his grandfather who lived in Hassan.

Haja Rao completed his elementary education in Hyderabad in a Muslim school. After matriculation he studied in the Nizam college where he met Ahmad Ali and his interest towards French rose, he even went to France to complete his higher education where he saw a great influence of Indian Literature on Irish literature. He was mamied to a French woman which did not last much long his depiction of the broken marriage is clearly depicted on the ‘Serpent and the Rope’ it was a semi-autobiographical novel which showed the search of spiritual truth in the Europe and India making him one of the finest writers of the country. This work also won him the prestigious Sahitya Academy award in 1964.

Raja Rao's first and one his best works Kanthapura is based on the south Indian village kanthapura. Themes like domination and oppression was seen in this work. It tells the story of a young Brahmin boy Moorthy who leaves his village to study in the city but after coming here he

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becomes familiar with the Gandhian philosophy and becomes very impressed with the culture and starts living like that. This causes the village priest excommunicate towards him. Saddened by this his mother dies and Moorthy starts to live with Ramanna a young widow who is educated; kamanna is also very active in the India's Struggle for independence.

The development of English as a impoaant medium of communication and language with accessible translations opened new doors for the Indian parents towards the western culture which made the Indian culture eclipsing its way.

Indian Writers in the Contemporary Period

India has been known for its multilingual nature and literature with more 22 official languages known has a history of more than 3000 written literature. Our literature is known for its vividness and variety in nature. The new generation has enlightened our nature with greater quality and variety. In the true sense it has represented our culture and its history in world wide. With number of Indian writers writing their work in English which makes our country third largest producer of novels after USA and UK. Although the writings are dealing with regionalism it has already crossed the boundaries of natural and universal themes. Indian writing is known for its complexity and depth in many themes like realism, globalization and modernity.

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Before diving into the diversifying world of the Indian contemporary literature it is very important to understand the terms of modern, modernity and modernization in the context of the Indian writing. The twentieth century is regarded as more modern in terms of the nineteenth century but that does not mean that the 19th century is excluded from the moden thinking. The distinct Indian English is very evident in the works of today's writers themes have not been limited to the tragedy and patriotism several other backgrounds, themes and new ideas has been included in their writing and Indianized English has been rehected in it. Regional languages like Bengali, Marathi, Kannad were freely used in the works of writers and Indian Idiom was also becoming popular among the Indian readers. Words like “sabash’ “ji Huzoor” etc were seen in the works of Mulk Raj Anand.

Salman Rushdie (1947- Present)

Salman Rushdie is one of the most promising writer of the modern contemporary writing in Indian writing. He has not only known to his country but has also enjoyed the global success through his writing. He is an Indian born American-British writer. His works often deal with the magic realism and historical fiction which shows connections disruptions and migration between the Eastern and westen civilizations mostly set in the Indian subcontinent. He was a son of the Cambridge educated lawyer and a teacher. He has three sisters; he grew up in Bombay and received his primary education from Cathedral and John Connan school in south Bombay before moving to England to attend Rugby school in Rugby

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His first novel Grimus a part science fiction tale which was published in 1975 failed to attract the reader's attention and the critics, although his next venture The Midnight's Children helped to gain him a global success and made him star overnight. This work helped him to gain Booker's prize in 1981 and 1993 to 2008 was awarded Best of the Bookers. After Midnight children he published Shame (1983) which showcased the political turmoil in Pakistan. Both his works showed us a style of magic realism and an immigrant outlook of the people. After that he wrote a book about Nicaragua named The Jaguar Smile which was based on the research and experiences of the Sandinista political experiments.

His most controversial work known as Satanic Verses was published in 1988 and was followed by Haroun and the sea of stories in 1990. It was written in the shadow of fatwa. It was based on the dangers of the story telling and an allegorical defence of power of stories over silence. Apañ from this work he has published many other short stories, children's books and other collections.

Anita Desai (1937- Present)

Anita Desai is another prominent writer of English. She is an Indian novelist and a professor of Humanities in Massachusetts Institute of Technology. She has been recipient of Sahitya Academy Award and have been nominated for the prestigious booker prize for three times. She has been appointed as the advisory committee of the Lalit kala Academy and a fellow of the Royal society of Literature London.

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Desai published her first novel Cry, the Peacock in 1963. Her another novel Clear light of day (1980) which she considers as highly autobiographical as it was

In 1984 she published her another work The custody it tells about an Urdu poet about his last declining days this work was shortlisted for the Booker prize. Her novel Fasting, Feasting helped her to gain global success and increased her popularity. Her next venture the zig zag way was set in the 20th century Mexico appeared in her last collection of shoa stories The artist of the Disappearance which was published in 2011. Her other works include Bye-Bye BlackbirdsVoices in the city, the peacock garden etc.

Khushwant Singh (1915- 2014)

A prominent figure in the contemporary English period was Khushwant Singh. He was an Indian author, diplomat, journalist and politician. The pWition of Índia and Pakistan inspired his work ‘the Train to Pakistan’ in 1956 which helped him to establish him as a well-known author. He was born in New Delhi was educated in the moden school and graduated from St. Stephan's college and Government College Lahore. He received his LLB from the University of London after working for eight years he retuned to Índia post-independence and joined the Indian Foreign Service. He was also appointed as the journalist in the All Tdia Radio in 1951 and moved to the Mass communication in UNESCO in Paris. These careers inspired him towards his literary career. As a writer he was known for his humour, sarcasm his unbiased secularism and his intense love for poetry.

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Out of his literary works 'Train to Pakistan' made him gain the international success. His another novel Delhi A novel was called as "History in the grab of Erotica" revolves around the history of Delhi. Another novel called India An introduction showcased India's rich cultural past to the present however it concentrates more about the land and the people from the earliest times. His other works like I shall not hear the Nightingale, Why I supported the emergency etc.

Vikram Seth (1952- Present)

An Indian author and poet known for his several novel and poetry books. He has been the recipient of many awards like the Sahitya Academy Awafds WH smith Academy award, Padma Shri and Crossword book cannon. His notable works like Mappings and Beasty Tales made him one of the prominent writers of the Indian writing. He was born in Calcutta his father worked for the Bata Shoes where his mother was a barrister and became the first Woman Judge in the Delhi High Court and first Chief justice of the State high couH in India.

Seth was known for publishing eight books of poetry and three novels. His first work Mappings was published in 1980. His next novel was The Suitable Boy which made him an overnight success which is also been adapted to a BBC Television mini-series in 2020. A sequel to the novel is announced in 2009. His another work Two lives was inspires a memoir of the mamiage of his great uncle and aunt. Seth was made a Commander of the order of the British Empire.

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Diaspora Writers

The dispersion of the people from the motherland; In simple words diaspora means the authors who are away from their native land and their works written by them. Diasporic Literature shows the longing the authors who are away from their mother land and their struggle for the nostalgia and finding for one's self. Majorly diasporic literature focuses on the displacement of the culture and amalgamation of the various things that takes in the same time. It also addresses the problem of immigration. Some of the important diasporic Indian writers are V.S Naipaul, Amitav Ghosh, Jhumpa Lahiri and Shashi Tharoor.

V.S Naipaul (1932- 2018)

V. S Naipual is an Indian Trinidadian British author who has published his works in both fiction and non-fiction. He was known for his humorous nature in novels set in Trinidad his understanding of the alienation from their roots. He also wrote prose work which sometimes rose some controversy. He published more than thirty books in his fifty years long career. He was born in Trinidad in the sugar plantation town of Chaguanas. His father was a journalist and used to write stories for the Trinidad Guardian and in 1932 he joined there as a staff of provincial Chaguanas correspondent. Naipaul's family moved to Trinidad when he was seven and permanently when he was nine.

Naipaul's novel 'A house for Mr. Biswas' was published in 1961 and it was considered as a break through

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work in his literary career which gained him immediate success. His early works described the ironical and satirical lives of the Caribbean the Mystic Masseur and The Suffrage of Elvira is an example of that. His works showed the character's stnggle for the longing of the native land and the problems of the alienation experienced in the new nations. His three novels in the Three state was set in various countries which won him The Booker prize and The bend in the river shows the unpredicted life of the new independent state. A way of the world is Naipaul's attempt to show that how history changes an individual's characters. His other works include The Mimic men and The enigma of the arrival.

Naipual won many awards for his works. He won The Booker Prize for In a free state in 1971. He won the Jensalem prize in 1983 and Trinity Cross in 1990. He was the recipient of the prestigious Nobel prize in literature in 2001 he was the second Indian who won this award after Rabindranath Tagore.

Jhumpa Lahiri (1967- Present)

Jhumpa Lahiri also Nilanjana Sudeshna was born in 1967 in London is an American author who is known for its short stories, essays and novels. She was born in an Indian family whose parents immigrated have immigrated from West Bengal to London. Their family moved to U.S when she was three years old Jhumpa Lahiri considers herself as an Ameücan as she grew up in Rhode Island where her father worked as a librarian in the University of the Rhode Island. Her work The third and the final Continent protagonist is

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inspired after her father. Lahiri's mother was very keen about her Bengali culture and insisted her children to have known to her roots they often visit their relatives in Calcutta.

LWiri faced rejections for her works from publishers for years. Her first short story collection Interpreter of Maladies was finally released in 1999. The work focuses on the sensitivities of the immigration of the Indian immigrants and struggle to adjust in the new life and other problems faced by them in the new life in a new country. This work gained her Pulitzer Prize in 2000 and sold 600000 copies of it. Her next novel The Namesake was published in 2003 and gained her a major success. The theme of the novel relates to the family story that she heard while growing up. The themes of the novel revolves immigration nostalgia of the native land and the cultural immigration. The novel was later adopted to be film directed by Mira Nair which was equally appreciated Even Jhumpa Lahiri made a cameo as ‘Aunty Jhumpa’ in the movie.

Her second collection of the shoJ stories was called Unaccustomed Earth was known for its well written fiction and gained number 1 position in The New York Times best seller list. Her works was also listed in the New Yorker Magazine she was known for short stories and non-fiction. She was also the winner of the DSC Prize for south Asian Literature for her work The Lowland for which she holds a limca book of records.

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Shashi Tharoor (1956-Present)

Shashi Tharoor is a former International diplomat, politician, writer and political diplomat who is also serving as a member of parliament as a member of Rajya Sabha from Kerala since 2009. He also served as a Under-secretary General of the United Nations and also ran for the post of Secretary General in 2006. He is also a chairman of the Parliamentary Standing Committee on Information Technology and All India Professional Congress and also served as the Chairman of the parliamentary standing committee on external affairs.

Tharoor was known to authored 23 works of fiction and non-fiction since 1981 which majorly focused on the rich Indian culture its heritage and other themes like film, politics, society foreign policy and many other themes. He is a recipient of the Sahitya Academy award For his work An Era of Darkness in a non-fiction category. He also worked as a columnist for the various newspaper in India and abroad in The New York Times, The Washington post, TME, Newsweek and The Times of India, He is also Lown for his rich vocabulary of English words. Tharoor staaed his literary career when he was six years old and his work also published in the Sunday edition of The Free Press Journal at the age of 10. His another work World War II adventure novel was about a RAF pilot which inspired the Biggles books also serialised in the Junior statesman. The great Indian novel also had 43 reprints as of October 2014 by Penguin India his another work the elephant the tiger and the cell phone also has several reprints. He has lectured widely about India and quoted that in his

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observations President Bill Clinton has also cited his book India from Midnight to the Millenium in his speech when he came to India. His major works include show business, riot, reasons of state, Nehru the invention of India and many others.

Amitav Ghosh (1956- Present)

Amitav Ghosh is one of the dynamic writers of the Indian English Writing. He was best known for his English language historical fiction. He is known for his ambitious novels that use complex narrative strategies that probe the nature of the national and personal identity particularly in the people of the India and south Asia. He is also known for discussing about the other topics in is non-fiction works as colonialism and slimate change. He received his elementary school in the Doon School in Dehradun and received his doctorate from University of Oxford in Social anthropology. He holds two life time achievement awards and four doctorate degrees. He is been the recipient of Jnanpith Award in 2018; India's highest literary honour. He was a joint winner of Dan David Prize with Margaret Atwood in 2010. He was the first Indian to win the Grand prix Award at Metropolis festival in in Montreal. He was also named as the most global thinkers of the preceding decade by the foreign policy magazine.

(1988), the Calcutta chromosome (1995) the glass palace (2000) etc. His debut novel was The circle of reason which was published in 1986. His first trilogy Ibis trilogy was set in 1830s just before the opium war which tells the story of the colonial history of the east, River of smoke was the

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second work of the trilogy and Flood of fire been the third. In 2021 he published his first verse Jungle nama which accounts the Sundarbans legend of Bon Bi.

Conclusion

Indian writing in English is also known as the Indo Anglican culture is the body of the writing which explores the writers who are Indian and writes in English. Since English is not our native language and it came to our country with the colonization of the Britishers and became the languages of the elites. In each era be it pre-Independence or post-independence Indian writers have proved their mettle in the field of writing and is responsible of generating new things in the English language writing. Rabindranath Tagore was the first non-European to win the Nobel prize in Literature and the legacy was taken forward by many other Indian Writers. Now India is the third largest producer of English writing after UK and USA.

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3. Women and Gender Study

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Introduction:

Women studies is an academic field that studies the feminine and interdisciplinary methods related to the women lives and experience and studies a them as a centre of study, while diving deep into the studies various aspects are kept in the mind like the social and cultural construction of gender; their privilege and oppression in the society and the relationship of power and gender as they often mix with other social identities such as race, culture , sexual orientation, ability many other disciplinary. It is an interdisciplinary field that explains that how gender affect the lives of individuals together with race, class, sexuality, ethnicity and ability. It draws its attention on other areas of social structure like anthropology, art, history literature, philosophy, political science, sociology and the visual arts. Women and gender studies about the various aspects that how a gender explains its past and present and its effect on the society as an individual and group levels it also studies the historical facts about the status of women and the factors that have changed the stature of women from various backgrounds to find better solutions to achieve the equality for all the people.

Many popular concepts are related to the field of woman studies which include feminist theory, standpoint

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theory, intersectionality, multiculturalism, transnational feminism, social justice, affect studies, agency, bio-politics, materialism, and embodiment. women studies is also connected to the field of gender studies, feminist studies and sexual studies and most importantly related to the cultural studies, ethnic studies and African- American studies. Women studies courses are available in many other countries in the world and more than seven hundred institutions in the United States and globally.

Status of Women in Different Ages and Gender Roles:

The status of women is very different in various ages and it varies from country to country. Traditionally women were considered as the home makers and men were considered as the bread winners. Women were expected as the care takers and their sole responsibility was to look after the chores of the house and look after the family. They were expected to look after the expenses of the family in the most economical way; they had to take care of all the age group of the family they have to obey to all the members of the family, but still considered as decisions of the second citizen of the family; they are often kept aloof from the major family and were not given the deserving respect in the family. Women were treated not equal by their own family majorly boys and men are treated superior in the family and were provided education and good belongings women were not provided proper education as it was considered as waste of money as they were married early and they have serve their in laws and thus doesn't require much education. There were other women who received

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education and changed the view of society towards women. This was only possible due to the support of their own families.

But the scenario has been changed in the recent times slowly but surely the status of women has been increased from the past now women have proved themselves in each and every field and the need and importance of them are equally felt. Not only that society has also changed their stand towards them due to the progress they have achieved for themselves it was possible because they took stand for themselves and came out of their comfort zones; this change can be termed as **"Women Empowerment".** Women have transformed their status from the past times now women are more multitasking and concentrated and serious about their respected careers. They are now more confident about themselves and equally participate in the decisions taken. Modern women of today are more confident of themselves and boldly participates in every affair and is bold about their views and opinions and is much aware of their rights and have created successful lives for themselves. Indira Nooyi, Sushmita Sen, Mother Teresa etc are the prime example of this.

Status of Women in the Ancient Times:

The state of women in the ancient period starts from the Vedic period which is spread from 300BC to 600 BC. Women enjoyed a respectable position in the ancient times; they were provided deserving respect in the society and were treated as equal to men they equally participated in the important decisions in the family matters. The amount

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of freedom that was provided to women in the ancient times is seen from the fact is that they were allowed to keep their opinions and views in every important matter in the house. There was no 'purdah system' in the early times women enjoyed full freedom in speech and clothing; even they had full freedom of selecting her own husband; however divorce was not permissible in those times men were not allowed to leave their wives and women enjoyed complete accessibility in the family matters.

Daughters were too treated with equals and provided education there was no discrimination between sons and daughters and they enjoyed every right what sons have. Daughters went through 'Brahmacharya' discipline including the 'upanayana' ritual and studied vedic literature along with men. And not only that some of them Ghosa, Sikata- Nivavari and Lopamudra were the authors of the vedic hymns. Many girls from the rich families and princesses were given fair amount of education in the vedic times.

Marriage was considered as a social and religious responsibility of the two individuals where women were allowed to choose their own life partners. Women were allowed to remain spinsters as marriage was not forcefully imposed to them; child marriages were unknown that time girls were married only after attaining puberty and that too completing her education. Love marriages were allowed that time and were known as "Gandharva Vivah". Monogamy was only form of marriage practise that time and widow re- marriage were allowed and a number of customs were practised which include 'Niyoga'; In this

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system where a brother or a deceased family of the nearest relative can marry the widow with taking permission of the family member. Rig Veda is considered to have the right of a spinster to inherit the right of having the father's right. Dowry was there but only subjective and was not compulsory.

Status of Women in the Medieval Times:

The middle period started from 5th century to 15th century between the fall of Roman empire and the Renaissance. It was a period that saw a great change in all spheres from construction of new buildings to pandemics. It was the age of the new ideas and new inventions many new ideas and concepts were discovered people started to think outside the church. Great thinkers like Galileo and Leonardo da Vinci were evident in this age. Majority of the people in the middle time were engaged in the agriculture including men and women. Women were educated but this was limited to the upper class women and clergy; nuns were educated to a certain limit. But there were significant women writers in that age who published and worked for the nobles at court.

With the changing times; the status of women also changed in the medieval times after the vedic period. The medieval times saw a lot of changes in the form of invasion and visits of the foreign investors the changes are equally felt. Women didn't enjoy the same amount of freedom in the medieval times as they enjoyed during the ancient times. Their life became harder as compared to the early times they had to work on the fields and take care of the household. Women lost the respect for themselves as they

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cannot participate themselves in any important matter. The system of ‘purdah’ was common among the muslims where they were prohibited to show their faces to other men. On the other hand Hindus practised the custom of Sati in which the widow had to immolate herself in the burning pyre of the husband.

During the Sultanate period the status of women decreased to a great extent for both Hindus and Muslims. Women were considered more of a commodity than an individual. They were not allowed to go outside and even were prohibited to go to the holy places as it was believed that if they went outside they might indulge themselves in some immoral activities. Polygamy was common in those days as it was taken as a part of honour to keep many women and even Rajputs killed their women and wives in order to save their honour when an army looses their wealth and belongings were distributed among the triumphant army among the women folk.

Status of Women in the Mordern Period:

Women in the modern times has changed drastically from the middle times and it can be said that it has improved a lot has been a topic of grave discussion; starting from the marital status to the right of education the empowerment of women has increased on a positive point. Women are now actively participating in every important matter in her life and society and making her presence and importance felt. But if we talk about the real picture about the status of women various social norms in one form or another still denies the importance of her part starting from the right to

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education to her health services. The social inequality hinders the development and growth of the society financial stability, global health and human rights and it becomes the major cause of poverty and hunger.

After the fall of the Mughal empire in the battle of plassey and the emergence of the British established their total supremacy in the Indians led to many economic and the political changes in the Indian society. Although the status of people remained more or less the same some mentioning changes were made in the field of employment education and eradication of the social evils. During this time a number of changes made in the economic and the social structure in the society. Some social evils like the sati system purdah system child marriage widow remarriage etc were controlled and removed by the legal legislations. These social evils were a great hindrance in the social development and growth in the society.

However the position was greatly improved after independence. Now becoming an independent nation it was easier to tackle the problems that confronted women. Social reformers and the British government helped to eradicate many social evils that proved hindrances in the position of the growth of the status of women. After a lapse of time after independence major changes can be seen in the areas like legislation, education employment and political participation etc. It can be said that at least after independence women were allowed to express their views to certain matters although it can't be said that it completely changed in their favour but the changes were commendable from the past times.

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Importance of the Women and Gender Studies:

With the changing world we have seen remarkable changes in the status of women from the past. But the scenario is not completely favourable in the case of women; still there are a lot of cases where we can see that women are still facing problems and inequality in the form of education, safety and other gender roles. Still death threats are received by them and this is not just the case of the under developed countries and poor countries but this happens in the developed nations as well. Their social life and rights are in a constant monitor by men and society they are still a subject of judgement and discussion. Constant threats about her life and social rights are in a target. Women are still expected to be multitasking as their main focus should be husband and family and are expected to compromise with their career. There are a number of issues that are faced by the women in the modern times:-

- Taking the sole responsibility of the household and nurturing of the children.
- Inequality in the household responsibilities
- Increasing rates of the marital mortality.
- Lack of love and respect deserved by the women
- Trauma centred feminism
- Not enough opportunities for women
- Not given importance in the major decisions taken in the family
- Compromise with her career.
- Unfriendly and judgement economic

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- Sexism, racism and economic inequality.

With the rising problems and inequality towards women shows a great need for the women studies. Even in the modern era women have to face too many problems and live in a constant fear of survival this study will help them to increase confidence in herself. Women studies came from the feminist movement which aims at changing and improving the status of women. Marilyn J. Boxer says "From the beginning, the goal of women studies was not merely to study but to change it"

Objectives of the Women and Gender Studies:

With the changing times the roles of women have changed. Now they are not only limited to household chores but now they are independent in themselves they are more confident in taking different roles for herself and proving them in the world. But with the changing times the threat for women is not minimised; there are constant cases where there are reports against brutality for women. The new age still can't accept the freedom that is provided to women. In many backward areas women are still tortured are not allowed to enjoy freedom as the males in the houses. They still have to be dependent for their rights.

The main aim of the women studies is to show the students to a substantial body of knowledge about the social construction of gender in the various cultural contexts from various disciplinary. It is characterized by the flexible, faculty monitored inter disciplinary plan of study designed to meet the need of the needs of the

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individual studies. It provides the students analytical tools to understand the lives, roles and experiences of women in different cultures to see women's status globally. The major objectives are:

- Analyze a systematic way in which we study the situation of women in our country and other countries from a variety of disciplinary perspectives.
- Analyze different ways in which gender, race, ethnicity, class etc construct social biological experience of both men and women.
- Recognize the masculinity dependence on the history of knowledge.
- To show and research women's experience in an unbiased manner.
- To show women's image in the literary texts, media, and the arts and explore the relations between these images and the attitudes of society towards women.
- Analyze systematic and institutional strategies of the exclusion and inclusion.
- To raise the awareness among the men and women by assisting them understanding, recognizing and acknowledgement in the different roles in the society.
- To support women in all the aspects of the society.

Role of Women in the Society:

Women are known as the primary care takers in the society in India and globally. They are expected to look after their homes and family in all around the world. A woman performs several roles in family and outside the world; she is a mother, daughter, sister, wife etc and so on. They are

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the pioneers of a nation; in order to create a healthy nation the need to give the deserving respect. Indian culture gives a great importance as they constitute half of the population. As per the report of the United Nations women constitutes half of the human resource in the world which is the next biggest human resource next to man. The different kind of roles a woman plays in a family and society.

- **As a wife** – the primary duty of a woman is expected to be a good wife to a man. She is a man's helpmate, partner and comrade. She sacrifices her desires and ambitions in order to look after her family. As a woman she is expected to compromise with her life and decisions. She is the source of inspiration for the high endeavour and achievements in his life.
- **As an administrator and leader of the household -** In order to create a disciplined household a woman's role is most important. She is the chief executive of the enterprise. She knows the abilities of all the people and distributes the work accordingly. She plans many recreational activities to meet the need of young and old members of the family.
- **As a mother-** the most important role of a woman is being a mother; she is the main basis of a new life. The whole burden of child bearing and greater part of child task is carried out by a woman.

She is the first teacher of a child. It is the mother who teaches the child about the laws of nature and the rules of the livelihood. Because of the intimate and sustained contact with the child she is able to discover the possibilities and abilities of the child and nurtures them accordingly and plays a key role in shaping the

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personality of a child. As a mother she is concerned about the well being of every member of the family. A woman devotes not only her time, thoughts and energy to her family but also nurtures it with love and dedication. For the unity of interacting personalities, man provides the temple and woman provides the atmosphere and the ceremonies.

Difference Between Women Studies Gender Studies and Feminism:

Feminism is a range of socio political movements and ideologies that aim to define and establish the facts about the rights of a woman and establish the political, economic, personal, and social equality of the sexes. Feminism incorporates the injustice done to women in the male dominated society where women are treated indifferently. Efforts are made to change this include fighting against the gender stereotypes and establishing educational, professional and interpersonal opportunities and outcomes for women who are equal to men.

The key difference between feminism and women studies is that women studies is a primarily focuses on women. It is a field of study which women are discussed anthropologically, sociologically, psychologically and historically, and how their roles have changed with time. It also delves in the culture intersectionality, studies and how women are treated and viewed in different cultures and societies. It includes theoretical framework which include feminism.

The main difference between women studies and gender studies is that woman studies primarily focuses on women while gender studies the woman studies, men

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studies and the queer studies. Woman studies in an interdisciplinary field that originated with the second wave of the women's movement in the late 1960s. Women studies mainly focuses on the growth, achievements and experiences of women in the society whereas the gender studies study both the genders in the whole and women studies is a part of the women studies. There are many fields that are connected with the women studies like the feminist theory, transnational feminism. Another major difference between the gender studies and women studies is their history, women's study began in 1960s and gender studies emerged out of woman studies.

Problems Faced by Women in Society

The world we live in is an ingrained social system that in all spheres is a male dominated society. A male dominated society is a place where the major rule makers are men they take all the major decisions in the society with patriarchal societal system and sadly there is a problem. The decision makers and the hierarchy beneath them is also males which makes a very less space for the women to make their presence felt. This situation is not only prevalent in particular under developed nations but this problem has now become more and will learn how to tackle them.

- **Discrimination-** With the changing times the status and roles have changed but sadly we can say there is complete improvement in the situation. Still there are many cases where we can see a woman is discriminated just because she is a woman. She is not only discriminated in her home but also in her

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workplace. Thousands of talented women have step back because of discrimination.

- **Domestic Violence-** This situation is a not a new problem in our society, women were treated as a commodity from the past times they were expected to bear the anger of the males of the family and the problem still exists. In order to empower women we need to make women feel safe at least in their homes.
- **Child Marriage-** this problem exists in our country where a woman is married before her marriageable age; this is a serious problem for not only for her health but also for the society as she will unable to produce a healthy offspring.
- **Gender Gap Pay-** women are expected to look after the homes and look after the family and their members but in the modern times women are not only home makers but also taking up different roles and fulfilling them successfully but still they have to face the gender gap pay because in the male dominated society it is believed that a woman only earns for herself and a man earns for the family so he needs to be paid more even though she do the same amount of work.

Conclusion:

Women are the integral part of the society and constitute half of the human population; they need to be nurtured and given respect. Women are seen as more compassionate than men and thus capable of taking care of their home effectively. Women in the early times enjoyed right amount of freedom and thus created a healthy environment, but with the changing times it became more like a male dominated society where all the major decisions were taken

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by men and it created a major imbalance in the society. Even in the modern times the situation has not completely changed in women's favour where the need of the Women Studies lies. In order to create a healthy environment firstly we have to create a safe environment for the women then only we have expected a bright future for all the individuals.

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