Statistical terpolymers with thermo-responsive fluorescent response in an ionic liquid: Effect of solvatophilicity on LCST phase separation and reversibility

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ABSTRACT

Well-defined terpolymers of benzyl methacrylate (BzMA), 9-(4-vinylbenzyl)-9H-carbazole (VBK) with either methyl methacrylate (MMA) or oligo(ethylene glycol)methacrylate (OEGMA) were synthesized to study their LCST-type phase behavior (due to BzMA) and fluorescent properties (due to VBK) in a hydrophobic ionic liquid IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([C_2mim][NTf_2] as a function of solvatophilicity and the difference in terpolymer chain mobility (via glass transition differences due to using MMA versus OEGMA). Specifically, MMA and OEGMA provided solvatophilic groups (the ester in MMA or ethylene glycol units in OEGMA) to the terpolymers and their composition was varied to study the effect of solvatophilicity on the terpolymer phase separation and re-dissolution processes in the IL. The concentration of solvatophilic groups in the terpolymer was not only shown to affect phase separation temperature significantly, but also demonstrated to be crucial in driving the re-dissolution process. A minimum concentration of solvatophilic groups to facilitate reversible phase separation was in the range of 20 – 30 mol% for both terpolymer systems. Solution concentration (1 – 10 wt%) also showed significant effects on phase separation temperature but lower concentration did not guarantee improved re-dissolution. Phase separation temperature was also demonstrated to be inversely proportional to polymer molecular weight (7.3 – 22.5 kg mol^{-1}). Lastly, the reversibility of phase separation and fluorescent responses in terpolymers with sufficient solvatophilicity was confirmed to be consistent by multiple heating/cooling cycles.

1. INTRODUCTION

In polymer-solvent systems, some polymers exhibit sharp changes in solubility in response to changes in temperature. Such thermo-responsive polymers in aqueous solutions have been widely studied because of their applicability to controlled drug delivery, bioseparations and tissue engineering.[1-4]

Ionic liquids (IL), which are molten organic salts, have drawn serious interest as versatile solvents because of their excellent chemical/thermal stability, ability to dissolve a broad range of compounds, non-volatility and non-flammability.[5-8] Numerous polymer/IL composite materials have been created to form ion gels as novel electrolytes for various electrochemical devices, eliminating flammability and leakage problems of conventional volatile solvent-based electrolytes.[9,10] A number of polymers were reported to be thermo-responsive in different ILs.[11-14] Among these polymers, poly(benzyl methacrylate) (PBzMA) was found to exhibit a sharp decrease in solubility upon being heated above a critical temperature (ie. lower critical solution temperature or LCST-type phase separation) in hydrophobic ILs.[12,15,16] The solvation of PBzMA in ILs was facilitated by spontaneous organization of the IL ions around the solvatophobic benzyl group of the polymer, resulting in a negative change in entropy upon mixing.[17,18] As temperature increased above a critical temperature, the ion layer around the benzyl group was disrupted by the increased freedom of motion, leading to phase separation.

To obtain sharp phase transitions and to study the effects of various factors (such as molecular weight and polymer composition) on the phase behavior, the polymer has to be well defined. For this reason, nitroxide mediated polymerization (NMP) was employed for this study. As one of the main controlled radical polymerization techniques, NMP controls polymerization through reversible termination of the propagating chains by the persistent nitroxide radical.[19,20] It is known that the homopolymerization of methacrylates such as BzMA is challenging for NMP mainly because of the very high equilibrium constant K which leads to large amount of active radicals and excessive termination.[21,22] Charleux et al.[21] reported that the average equilibrium constant <K> could be significantly reduced when methyl methacrylate was copolymerized with a small amount of co-monomer that has a much lower K such as styrene and controlled synthesis of methacrylate-rich copolymers could be achieved using the commercially available initiator BlocBuilder^{TM}. Since then, numerous methacrylate-rich copolymers have been polymerized in controlled manners by NMP using a small amount of styrene and other controlling co-monomers.[23-26]

In our previous study,[27] BzMA was combined with a fluorescent co-monomer, 9-(4-vinylbenzyl)-9H-carbazole (VBK), in random copolymers. VBK has been demonstrated previously to be an effective controlling co-monomer for a number of methacrylate-rich copolymerizations via NMP.[28-30] The combination of thermo-responsiveness and fluorescent properties was aimed to create materials potentially useful for sensing, imaging or actuator applications.[31-33] Interestingly, the fluorescence intensity of the BzMA/VBK copolymers in a hydrophobic IL increased sharply 5-fold as phase separation occurred.[27] Emission/excitation spectra as well as Raman spectra of IL solutions of BzMA homopolymer and BzMA/VBK copolymers indicated that BzMA and VBK were likely a fluorescence resonance energy transfer (FRET) donor and acceptor pair.[27] The increased proximity between BzMA and VBK units during phase separation greatly enhanced FRET efficiency and resulted in fluorescence enhancements.[27,34] This increase in fluorescence intensity in response to the temperature change made the copolymers interesting candidates as novel fluorescent molecular thermometers.[31,32,35,36] These molecular thermometers can be used to measure micro-sized areas (eg. biological cells), to map two- or three-dimensional temperature distribution, or to monitor temperature in harsh environments (eg. highly corrosive or high voltage) where conventional thermometers are not practical.[32,35,36] To be useful for these applications, the fluorescent response of the system has to be reversible and highly consistent. However, the incorporation of solvatophobic VBK in the BzMA/VBK copolymers rendered the phase separation and hence the fluorescence enhancement of the copolymers completely irreversible.

The reversibility of the phase transition of polymer/IL systems has not been studied widely. The phase separation of PBzMA in hydrophobic ILs was reported to be reversible with very slow re-dissolution kinetics.[16] By modifying the polymer structure to adjust the solvatophilic/solvatophobic balance, Kodama et al. were able to significantly alter the re-dissolution rate.[16] In addition, they also found that a larger difference between phase separation temperature and glass transition temperature (T_g) of the polymer generally led to faster re-dissolution. Their study about the reversibility of the PBzMA and its derivatives in the IL solutions was intriguing but reversibility can be affected by other factors such as molecular weight and solution concentration. Therefore, a more comprehensive study was needed to provide more insight to the re-dissolution process. Also, to tune the solvatophilic/solvatophobic balance, instead of modifying each polymer structure, a more intuitive approach would be simply adjusting the composition of a copolymer with a solvatophilic and a solvatophobic co-monomer. With this approach, the solvatophilic/solvatophobic ratio of the copolymer can be quantified and finely tuned.

Therefore, in this study, terpolymers consisting of BzMA, VBK and a solvatophilic co-monomer with different compositions were synthesized using NMP and their phase behavior was studied in a hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ($[C_2mim][NTf_2]$).

Homopolymers of methyl methacrylate (MMA) and oligo (ethylene glycol) methacrylate (OEGMA) are both known to be soluble in $[C_2mim][NTf_2]$.[15,37,38] However, PMMA has a higher T_g than PBzMA while the T_g of POEGMA is much lower than that of PBzMA.[27,39] T_g of a polymer plays an important role in polymer dynamics during the dissolution process and thus also significantly affects the re-dissolution of the phase separated-polymer during cooling.[16,40] As the content of MMA or OEGMA was increased in the terpolymer, both of the BzMA/MMA/VBK and BzMA/OEGMA/VBK terpolymers should exhibit improving solubility in the IL but the former would have increasing T_g whereas the latter would have decreasing T_g. This study attempts to determine how the T_g of the terpolymers affects their phase behavior and dynamics in the IL, given that solubility is similar. The synthesis of these terpolymers will be first addressed, followed by detailed investigations of the effects of polymer composition, solution concentration, and molecular weight on terpolymer phase behavior and fluorescence responses in the IL.

2. EXPERIMENTAL SECTION

2.1 Materials

N,N-Dimethylformamide (DMF, 99.8%), benzyl methacrylate (BzMA, 96%), methyl methacrylate (MMA, 99%), oligo(ethylene glycol) methyl ether methacrylate (OEGMA, average molecular weight = 475 g mol^{-1}), basic alumina (Brockmann, Type I, 150 mesh), and calcium hydride (90-95% reagent grade) were purchased from Sigma-Aldrich; tetrahydrofuran (THF, 99.9%) was obtained from Fisher; deuterated chloroform ($CDCl_3$) was obtained from Cambridge Isotope Laboratories Inc. BzMA, and MMA monomers were purified by passing through a column of basic alumina mixed with 5 wt% calcium hydride; they were stored in a sealed flask under a head of nitrogen in a refrigerator until needed. All other compounds were used as received. 2-((*tert*-butyl[1-(diethoxyphosphoryl)-2,2-(dimethylpropyl]amino)oxy)-2-methylpropionic acid, also known as BlocBuilder^{TM} (99%), was purchased from Arkema; (tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino) nitroxide (SG1, >85%) was kindly donated by Noah Macy from Arkema, both were used as received and stored at 5 °C. Ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2mim][NTf_2], 99%) was purchased from Iolitec; it was used without further purification and stored in a desiccator to minimize moisture exposure. 9-(4-Vinylbenzyl)-9H-carbazole (VBK, >95%) was synthesized according to previous literature.[41]

2.2 Terpolymerization of benzyl methacrylate (BzMA), methyl methacrylate (MMA) or oligo(ethylene glycol) methyl ether methacrylate (OEGMA) ,and 9-(4-Vinylbenzyl)-9H-carbazole (VBK)

The terpolymerizations were performed in a 50 mL three-neck round-bottom glass flask fitted with a reflux condenser, a magnetic stir bar, and a thermal well. The amounts of initiator and monomers were calculated according to a target molecular weight ($M_{n,target}$, theoretical molecular weight at 100% conversion) of 15, 40 or 80 kg mol^{-1}.

Feed composition of VBK ($f_{VBK,0}$, mol%) was fixed at 10 mol% while the feed composition of BzMA ($f_{BzMA,0}$, mol%) was varied from 50 to 80 mol% for BzMA/MMA/VBK terpolymerizations and varied from 80 to 87 mol% for BzMA/OEGMA/VBK terpolymerizations; *N,N*-dimethylformamide (DMF) was also added (solution concentration 20 wt%) to assist dissolution of VBK. Detailed experimental conditions were summarized in Table 1. Using the experiment B80/M10/V10-40 as an example, a mixture of BlocBuilder (0.0576 g, 0.15 mmol), SG1 (0.0044 g, 0.015 mmol), BzMA (4.75 g, 0.027 mol), MMA (0.35 g, 0.0035 mol), VBK (0.90 g, 0.0034 mol) and DMF (24.3 g) was added to the reactor. The solution was then deoxygenated by nitrogen bubbling for 30 min at room temperature prior to heating to 90 ^{o}C at a rate of about 8 ^{o}C min^{-1} while maintaining a nitrogen purge. The time when the solution reached 90 ^{o}C was taken as the start of the reaction (t = 0). Samples were taken periodically to determine conversion and molecular weight. Monomer conversion was estimated gravimetrically. ^{1}H NMR was not used to determine conversion because of overlapping peaks of the three monomers. Terpolymer composition was determined by ^{1}H NMR (400 MHz Varian Gemini 2000 spectrometer, $CDCl_3$). The ^{1}H NMR spectra of a BzMA/MMA/VBK terpolymer (using B60/M30/V10-40 as example) and a BzMA/OEGMA/VBK terpolymer (using B85/O5/V10-40 as example) are shown in Figure 1. The terpolymer product was precipitated in methanol, decanted and dried in vacuum at 40 ^{o}C overnight to give 1.68 g of B80/M10/V10-40 (yield = 28% (low yield mainly due to loss of polymers in samples), overall conversion = 39%, number-average molecular weight M_n = 13.2 kg mol^{-1} and dispersity Đ = 1.35). Molecular weight and dispersity of the samples were measured using GPC (Waters Breeze) (see ***Gel Permeation Chromatography*** section for full details). The molecular weight stated for the terpolymers was relative to poly(methyl methacrylate) standards in THF at 40 ^{o}C. The glass transition temperatures (T_g) of the terpolymers were determined using differential scanning calorimetry (DSC). The measurements followed a standard heat/cool/heat protocol where sample was first heated to 150 ^{o}C, then cooled to – 20 ^{o}C and finally heated to 150 ^{o}C again, at a rate 10 ^{o}C/min in all cycles. The T_g was defined as the inflection point on the heating curve during the second heating.

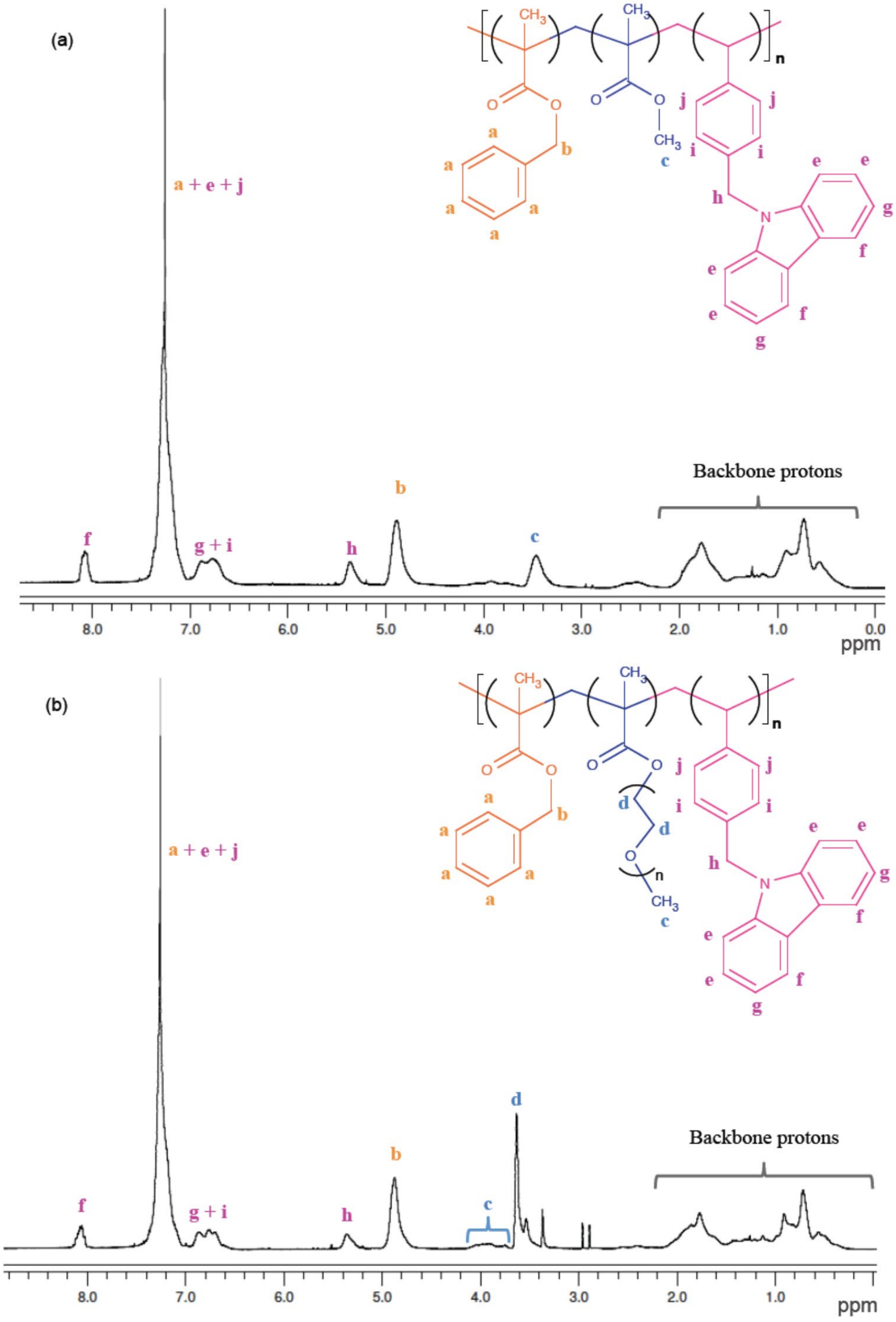

Figure 1: ^{1}H NMR spectrum of (a) B60/M30/V10-40 as an example of BzMA/MMA/VBK terpolymer and (b) B85/O5/V10-40 as an example of BzMA/OEGMA/VBK terpolymer.

2.3 Gel permeation chromatography

Molecular weight and dispersity (Đ) of all polymers were characterized by gel permeation chromatography (GPC) (Waters Breeze) using THF as the mobile phase at 40 °C in this study. The GPC was equipped with three Waters Styragel HR columns (molecular weight measurement ranges: HR1: $10^2 - 5 \times 10^3$ g mol^{-1}, HR2: $5 \times 10^2 - 2 \times 10^4$ g mol^{-1}, HR3: $5 \times 10^3 - 6 \times 10^5$ g mol^{-1}) and a guard column. The columns were operated at 40 °C and a mobile phase flow rate of 0.3 mL min^{-1} during analysis. The GPC was also equipped with both ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors. The results reported in this paper were obtained from the RI detector. All molecular weight measurements were calibrated with poly(methyl methacrylate) narrow molecular weight distribution standards in THF at 40 °C.

Table 1: Experimental conditions for terpolymerizations of benzyl methacrylate (BzMA), methyl mathacrylate (MMA) or oligo(ethylene glycol)methyl methacrylate (OEGMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK) in dimethylformamide (DMF) solution at 90 °C via NMP

Expt. ID[a]	[BlocBuilder]	[SG1]	[BzMA]	[MMA] or [OEGMA]	[VBK]	[DMF]	$M_{n,target}$
	mmol L^{-1}	mmol L^{-1}	mol L^{-1}	mol L^{-1}	mol L^{-1}	mol L^{-1}	kg mol^{-1}
B80/M10/V10-40	4.9	0.5	0.883	0.115	0.109	10.9	40.1
B70/M20/V10-40	5.0	0.5	0.812	0.228	0.115	10.9	40.1
B60/M30/V10-40	5.0	0.5	0.725	0.360	0.121	10.9	39.9
B50/M40V10-40	5.0	0.5	0.632	0.508	0.127	10.9	39.9
B80/M10/V10-15	13.5	1.3	0.883	0.115	0.097	10.9	14.9
B80/M10/V10-80	2.5	0.3	0.888	0.111	0.109	10.9	78.1
B87/03/V10-40	4.9	0.5	0.877	0.031	0.100	10.9	40.2
B85/05/V10-40	4.9	0.5	0.831	0.051	0.097	10.9	40.1
B83/07/V10-40	4.9	0.5	0.784	0.065	0.096	10.9	40.1
B80/010/V10-40	4.9	0.5	0.724	0.094	0.091	10.9	40.2

[a] The experiment ID Bx/My/Vz-m (or Bx/Oy/Vz-m) denotes feed composition in mol% of BzMA (B), MMA (M) or OEGMA (O) and VBK (V) with x, y, z, with respectively, m represents the target molecular weight which is the number average molecular weight at 100% conversion

2.4 Characterization of the ionic liquid solutions of the terpolymers

The terpolymers were dissolved in the ionic liquid 1-ethyl-3-methylimmidazolium bis(trifluoromethylsulfonyl)imide ($\mathrm{[C_2mim][NTf_2]}$) with THF as the co-solvent. THF was subsequently evaporated at atmospheric pressure and room temperature for 24 hours followed by drying in vacuum at about 60 °C until constant weight was measured.

Solution concentration was varied from 1 - 10 wt% and the solutions were stored in a desiccator to minimize exposure to moisture. The transition temperature of the terpolymer solutions was characterized using a Cary 5000 UV-vis-NIR Spectrophotometer. Light transmittance of the solutions was monitored at 600 nm while the solution is heated/cooled at a rate of 1 °C min^{-1}. The cloud point temperature is defined as the temperature where the transmittance dropped to 50% during heating. Fluorescence measurements were performed using a Cary Eclipse fluorescence spectrophotometer equipped with a xenon flash lamp and Peltier thermostated multi-cell holder with a temperature controller. Solutions were excited at a wavelength of 330 nm in quartz cuvettes at various temperatures and their emission spectra were recorded.

3. RESULTS AND DISCUSSION

3.1 Terpolymerization kinetics and polymerization control

Terpolymerizations of benzyl methacrylate (BzMA), 9-(4-vinylbenzyl)-9H-carbazole (VBK) and methyl methacrylate (MMA) or oligo(ethylene glycol)methyl methacrylate (OEGMA) were performed with feeds containing fixed amount of VBK (10 mol%) and varying BzMA:MMA (from 80:10 to 50:40) or BzMA:OEGMA (from 87:3 to 80:10) compositions. Results including conversion, composition, molecular weight and dispersity (Đ) were summarized in Table 2.

Table 2: Summary of characterization data for terpolymers of benzyl methacrylate (BzMA), methyl methacrylate (MMA) or oligo(ethylene glycol)methyl methacrylate (OEGMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK) synthesized at 90 °C in 20 wt% DMF solution

Expt. ID[a]	Polym. time	Conv.[b]	F_{BzMA}[c]	F_{MMA}[c] or F_{OEGMA}[c]	F_{VBK}[c]	M_n[d]	Đ[d]
	min		mol%	mol%	mol%	kg mol^{-1}	
B80/M10/V10-40	245	39%	74%	10%	16%	13.6	1.32
B70/M20/V10-40	243	38%	65%	18%	17%	15.3	1.36
B60/M30/V10-40	261	39%	60%	22%	18%	17.8	1.30

B50/M40V10-40	245	46%	51%	29%	20%	14.1	1.28
B80/M10/V10-15	258	36%	75%	9%	16%	7.3	1.30
B80/M10/V10-80	360	47%	77%	9%	14%	22.5	1.44
B87/03/V10-40	303	40%	88%	2%	10%	14.3	1.37
B85/05/V10-40	302	37%	86%	3%	11%	13.4	1.33
B83/07/V10-40	304	39%	81%	5%	14%	15.4	1.36
B80/010/V10-40	300	41%	79%	7%	14%	16.0	1.35

[a] The experiment ID Bx/My/Vz-m (or Bx/Oy/Vz-m) denotes feed compositions of BzMA (B), MMA (M) or OEGMA (O) and VBK (V) in molar percentage with x, y, z, with respectively, m represents the target molecular weight which is the number average molecular weight at 100% conversion; [b] Final conversion estimated by gravimetry; [c] Final terpolymer composition determined by ^{1}H NMR; [d] Number average molecular weight and polydispersity index of the copolymer measured by GPC relative to poly(methyl methacrylate) standards in THF at 40 °C.

VBK was previously reported to be effective in controlling methacrylate-rich copolymerizations via NMP.[23,28,30] In this study, VBK was not only used as a controlling co-monomer, but also to impart fluorescent properties to the terpolymer due to its carbazole moiety, which will be discussed in Section 3.2.4.

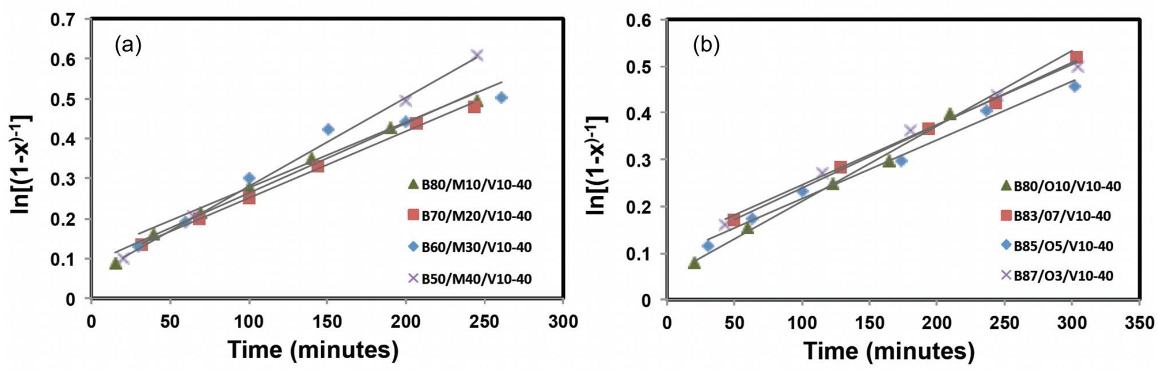

Figure 2: Semi-logarithmic kinetic plots of terpolymerization of (a) benzyl methacrylate (BzMA) methyl methacrylate (MMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK), and (b) benzyl methacrylate (BzMA) oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK) at 90 °C via NMP.

All terpolymerizations were conducted typically for about 4 – 6 hours and the final overall conversion ranged from 36% to 47%. The kinetics of the terpolymerizations was illustrated by semi-logarithmic plots of ln[(1-conversion)$^{-1}$] versus time in Figure 2. First order kinetics was observed for all terpolymerizations, as expected for controlled polymerizations. Small deviations from the linear trends were observed in some cases. The downward deviations towards the end of the terpolymerizations was also observed for the BzMA/VBK copolymerizations previously reported,[27] which could be due to chain transfer to the monomers or the solvent. A couple of data points from B60/M30/V10-40 also showed deviation from the linear trend, likely resulting from overestimation of conversion when using gravimetry, which is known to cause frequent overestimation of conversions.[42,43]

The apparent rate constant $\langle k_p \rangle[P\bullet]$, which is the product of average propagation rate constant $\langle k_p \rangle$ and propagating radical concentration $[P\bullet]$, was estimated using the slope from the kinetic plots and summarized in Table 3. For BzMA/MMA/VBK terpolymerizations, their $\langle k_p \rangle[P\bullet]$ ranged from 2.7 x 10^{-5} s^{-1} to 3.7 x 10^{-5} s^{-1}; for BzMA/OEGMA/VBK terpolymerizations, their $\langle k_p \rangle[P\bullet]$ ranged from 2.1 x 10^{-5} s^{-1} to 2.7 x 10^{-5} s^{-1}. There was no obvious correlation between the reaction rate and the feed composition in either case. Feed composition did not affect the kinetics significantly. These results were expected since the reported $\langle k_p \rangle[P\bullet]$ values of the binary copolymerizations of these methacrylates with a small amount of VBK were comparable: $\langle k_p \rangle[P\bullet]_{BzMA/VBK}$ = 1.9 x 10^{-5} s^{-1} (with $f_{VBK,0}$ = 11 mol%),[27] $\langle k_p \rangle[P\bullet]_{MMA/VBK}$ = 4.3 x 10^{-5} s^{-1} (with $f_{VBK,0}$ = 5 mol%),[44] and $\langle k_p \rangle[P\bullet]_{OEGMA/VBK}$ = 1.0 x 10^{-5} s^{-1} (with $f_{VBK,0}$ = 10 mol%),[30] all estimated at 90 °C in dimethylformamide solutions, which were the same conditions as those used for the terpolymerizations in this study.

Table 3: Feed composition and the product of average propagation rate constant, $\langle k_p \rangle$, and propagating radical concentration, $[P\bullet]$, $\langle k_p \rangle[P\bullet]$, for terpolymerizations of benzyl methacrylate (BzMA), methyl methacrylate (MMA) or oligo(ethylene glycol)methyl methacrylate (OEGMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK).

Expt. ID	$f_{BzMA,0}$[a]	$f_{MMA,0}$ or $f_{OEGMA,0}$[a]	$f_{VBK,0}$[a]	$\langle k_p \rangle[P\bullet]$[b]
	mol%	mol%	mol%	$s^{-1} \times 10^5$
B80/M10/V10-40	80%	10%	10%	2.92 ± 0.15
B70/M20/V10-40	70%	20%	10%	2.79 ± 0.06
B60/M30/V10-40	60%	30%	10%	2.74 ± 0.37
B50/M40V10-40	50%	40%	10%	3.71 ± 0.07
B87/03/V10-40	87%	3%	10%	2.15 ± 0.13
B85/05/V10-40	85%	5%	10%	2.09 ± 0.11

B83/07/V10-40	83%	7%	10%	2.24 ± 0.06
B80/010/V10-40	80%	10%	10%	2.69 ± 0.10

[a] Feed compositions; [b] Estimated using the slopes of the kinetic plots shown in Figure 1.

The level of control for the terpolymerizations was also illustrated by the linear increase in the number-average molecular weight (M_n) versus conversion shown in Figure 3. The dispersity (Đ) of the terpolymers was between 1.2 to 1.4.

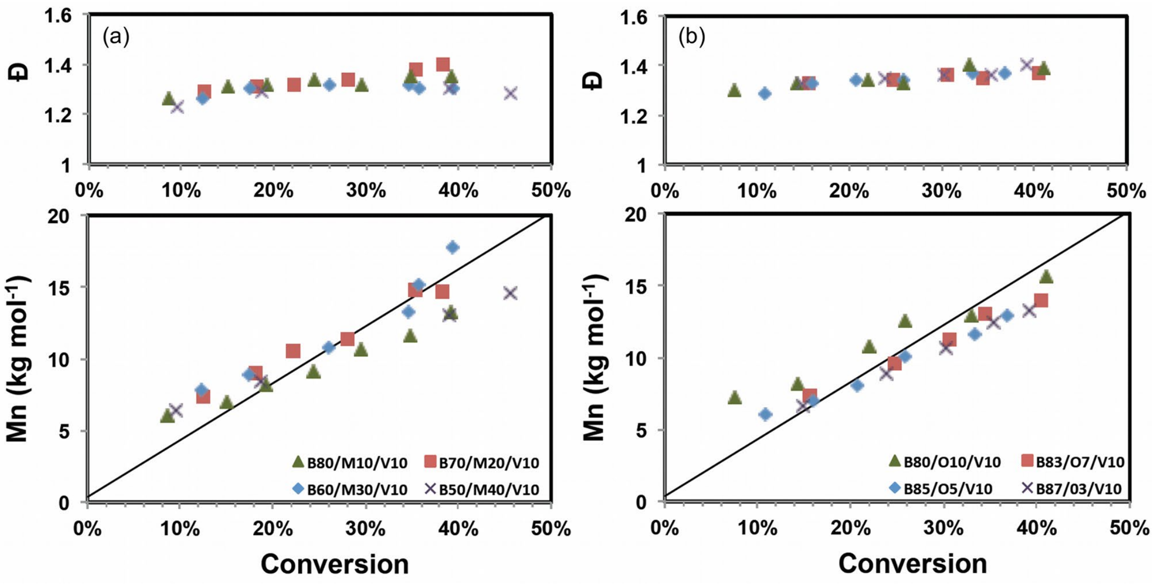

Figure 3: Number-average molecular weight (M_n) and dispersity (Đ) of terpolymers of (a) benzyl methacrylate (BzMA), methyl methacrylate (MMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK), and (b) benzyl methacrylate (BzMA) oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and 9-(4-vinylbenzyl)-9H-carbazole (VBK), measured by GPC calibrated with poly(methyl methacrylate) standards. The linear lines in the M_n versus conversion graphs represent the theoretical trends.

It is also interesting to note that the terpolymer compositions were quite different from the feed compositions, especially for BzMA/MMA/VBK terpolymers. The terpolymers were significantly richer in VBK and less rich in MMA compared to their feed compositions, while terpolymer composition and feed composition of BzMA remained similar. While the factors affecting relative reactivities of 3 co-monomers can be complicated, these results were not surprising. VBK was reported to show strong preference to react with its own radical than to MMA radicals (reactivity ratios of

MMA/VBK were calculated to be 0.2 and 2.7, respectively[28]). In OEGMA/VBK copolymerizations, copolymer compositions were also measured to be richer in VBK than OEGMA compared to feed compositions as the feed composition was varied between 95 mol% and 80 mol% OEGMA.[30] On the other hand, significant composition shifts were not observed for BzMA/VBK copolymerizations.[27] The narrow range of feed composition variance for BzMA/OEGMA/VBK may limit the composition shifts for those terpolymerizations as all the feeds were rich in BzMA.

In summary, the kinetics and M_n increases of the terpolymerizations of BzMA/MMA/VBK and BzMA/OEGMA/VBK matched those expected from controlled polymerizations and terpolymer compositions were reasonable based on literature data.

3.2 Temperature sensitivity and fluorescence properties of terpolymers in [C_2mim][NTf_2]

One of the main objectives of this study was to comparatively investigate the solution properties of the BzMA/MMA/VBK and BzMA/OEGMA/VBK terpolymers in the IL [C_2mim][NTf_2].

PBzMA is known to exhibit lower critical solution temperature (LCST)-type phase separation in [C_2mim][NTf_2].[12,16,27] We previously reported that the incorporation of solvatophobic VBK in random copolymers with BzMA not only led to decreased solubility and hence lower LCST in the IL as expected, but also rendered the phase separation of the random copolymers irreversible.[27] However, the copolymers of BzMA and VBK exhibited a very interesting fluorescence enhancement triggered by phase separation.[27] In order to restore the reversibility of the thermo-responsiveness of BzMA-rich copolymers while keeping the fluorescence properties of VBK, MMA or OEGMA, whose homopolymers are both completely soluble in [C_2mim][NTf_2],[15,37,38] were incorporated to increase the solubility[29,30] and hence improve reversibility of the terpolymers. The effects of copolymer composition, solution concentration and molecular weight on the phase separation transition and reversibility as well as fluorescence properties of these terpolymers in [C$_2$mim][NTf$_2$] will be further discussed in detail in the following sections.

The composition, molecular weight and glass transition temperature of all the terpolymers as well as their cloud point temperature (CPT) were summarized in Table 4.

Table 4: Summary of polymer composition, number average molecular weight, glass transition temperature and cloud point temperature (CPT) in [C$_2$mim][NTf$_2$] (3 wt% concentration) of the terpolymers

Polymers[a]	F_{BzMA}	F_{MMA} or F_{OEGMA}	F_{VBK}	M_n[b]	T_g[c]	CPT[d]
	mol%	mol%	mol%	kg mol^{-1}	°C	°C
B80/M10/V10-40	74%	10%	16%	13.6	76	62
B70/M20/V10-40	65%	18%	17%	15.3	83	71
B60/M30/V10-40	60%	22%	18%	17.8	85	79
B50/M40V10-40	51%	29%	20%	14.1	89	95 (82)
B80/M10/V10-15	75%	9%	16%	7.3	67	84
B80/M10/V10-80	77%	9%	14%	22.5	80	55
B87/O3/V10-40	88%	2%	10%	16.0	70	69
B85/O5/V10-40	86%	3%	11%	15.4	64	84 (59)
B83/O7/V10-40	81%	5%	14%	13.4	55	97 (84)
B80/010/V10-40	79%	7%	14%	14.3	45	N/A[e]

[a] Refer to Table 1 for the synthesis conditions for these terpolymers; [b] Number average molecular weight of the copolymer measured by GPC relative to poly(methyl methacrylate) standards in THF at 40 °C; [c] Glass transition temperature of terpolymers measured by differential scanning calorimetry (DSC); [d] Cloud point temperature (CPT) defined by the temperature where 50% light transmittance was recorded during heating, the numbers in brackets are temperatures where 50% light transmittance was obtained during cooling; phase separation was irreversible if only one temperature was listed; [e] Solution remained clear up to 100 °C (upper temperature limit of the instrument)

3.2.1 Effect of varying solvatophilic content in terpolymers on transition temperature and reversibility

The effect of varying solvatophilic content (ie. F_{MMA} or F_{OEGMA}) on phase separation temperature and reversibility was a key objective of this study. The terpolymers mentioned in this section were all synthesized with the same target molecular weight (40 kg mol^{-1} at complete conversion) and had similar molecular weight (ranged from 13.4 to 17.8 kg mol^{-1}). Therefore, the variation of polymer composition was considered to be the dominant factor affecting the solution properties of these terpolymers. The light transmittance of these terpolymer solutions in [C_2mim][NTf_2] as temperature was varied is shown in Figure 4, where 100% light transmittance indicates a transparent solution.

The first observation was that with increasing solvatophilic content in the terpolymer, phase separation occurred at higher temperatures. This is consistent with the use of solvatophilic co-monomers in a thermo-responsive polymer to increase copolymer solubility and LCST in both aqueous[29,30] and IL[12] solutions. The increase in CPT versus terpolymer composition of the solvatophilic co-monomer (ie. F_{MMA} or F_{OEGMA}, Figure 5 (a)) may appear that MMA and OEGMA had very different impacts on the solvatophilicity of the terpolymers. However, one should take note that for each MMA monomer, there is one solvatophilic group, namely the ester group;[16] whereas for each OEGMA monomer, there are multiple ethylene glycol (EG) units (~8.5 EG per OEGMA monomer in this case based on the average M_n of OEGMA used). Although the correlation between the number of EG units and polymer solubility in ILs has not been comprehensively studied, Horton et al. showed that the higher the number of EG units, the better the solubility of poly(methoxyoligo(ethylene glycol) methacrylates was in [C_2mim][NTf_2]-saturated water.[45] It is also well known that poly(ethylene glycol) is completely soluble in [C_2mim][NTf_2].[46,47] Therefore, to make a better comparison of solvatophilicity between MMA and OEGMA co-monomers, the effect of terpolymer composition of MMA and that of EG units of the corresponding OEGMA on the cloud points were compared in Figure 5 (b). It shows that there exist similar effects of the concentration of solvatophilic groups in a polymer on the solvatophilicity of the overall polymer. This is interesting since one of the reasons why OEGMA and MMA were chosen as the solvatophilic co-monomers was that they have very different glass transition temperatures (T_g) and thus different polymer dynamics during dissolution. T_g of POEGMA (~ -70 ^oC[39,48]) is much lower compared to PMMA (105 ^oC[39]). T_g of PBzMA is about 54 ^oC[39] and a random copolymer of BzMA and VBK with ~ 10 mol% VBK had a T_g of about 66 ^oC.[27] Therefore, the incorporation of MMA increased the overall T_g of the BzMA/MMA/VBK terpolymers (from 76 to 89 °C as F_{MMA} increased from 10 to 29 mol%) whereas the OEGMA content in the BzMA/OEGMA/VBK decreased the terpolymer T_g (from 70 to 45 °C as F_{OEGMA} increased from 2 to 7 mol%). Despite the higher T_g of the BzMA/MMA/VBK terpolymers, their CPTs were comparable to those of

BzMA/OEGMA/VBK terpolymers with similar concentration of solvatophilic group but lower T_g. It indicated that the concentration of solvatophilic groups was a dominant factor affecting the cloud point of the terpolymer in the solution.

In some cases of thermo-responsive polymers with a solvatophilic comonomer, the phase separation of the copolymers can become sluggish or the copolymers can even completely lose their thermo-responsiveness.[23,29,49] With up to F_{MMA} = 29 mol% (B50/M40/V10-40) for the BzMA/MMA/VBK terpolymers or F_{OEGMA} = 5 mol% (or $F_{EG\ unit}$ = 31 mol%, B83/O7/V/10-40) for the BzMA/OEGMA/VBK terpolymers, the decrease in light transmittance as the solutions were heated above the CPT was sharp in all cases. Since the heating rate remained the same, it means that the introduction of solvatophilic MMA or OEGMA did not significantly affect the aggregation kinetics within the composition range studied.

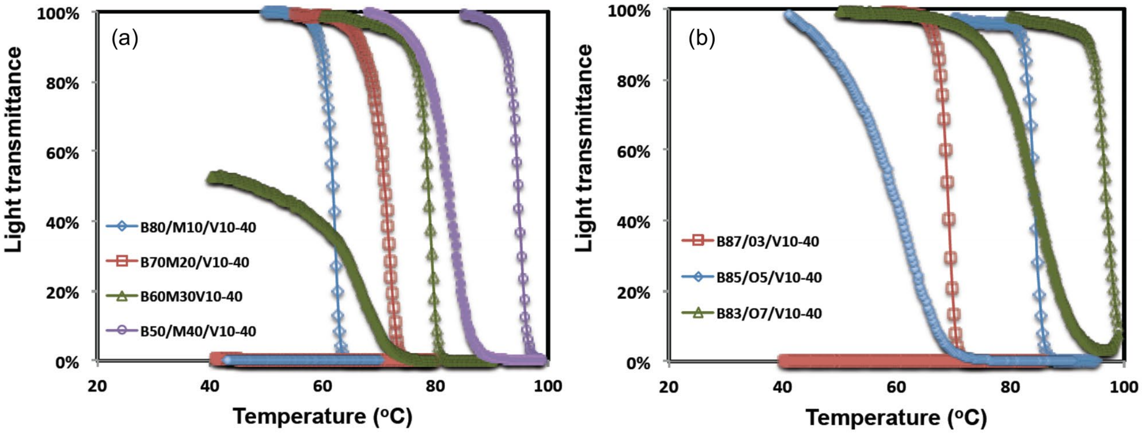

Figure 4: Light transmittance of 3 wt% terpolymer in ionic liquid solutions of (a) BzMA/MMA/VBK terpolymers, and (b) BzMA/OEGMA/VBK terpolymers with heating/cooling rate of 1 °C min^{-1} (heating cycles with hollow symbols and cooling cycles with solid symbols).

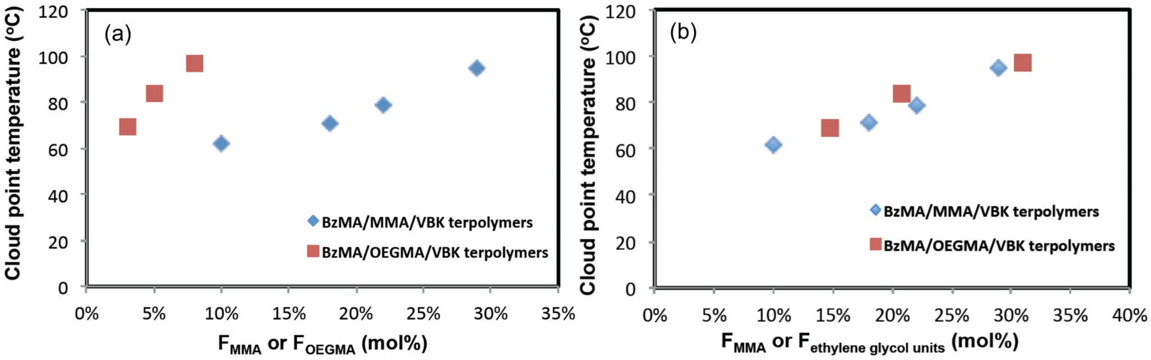

Figure 5: Cloud point temperature of 3 wt% solutions of BzMA/MMA/VBK (blue diamonds) and BzMA/OEGMA/VBK terpolymers (red squares) versus (a) terpolymer composition of MMA (F_{MMA}) or terpolymer composition of OEGMA (F_{OEGMA}); (b) terpolymer composition of MMA (F_{MMA}) or terpolymer composition of ethylene glycol units ($F_{ethylene\ glycol\ units}$, calculated by ($F_{OEGMA}$ x 8.5)/(F_{BzMA}+F_{VBK}+F_{OEGMA} x 8.5) x 100%, 8.5 being the average number of ethylene glycol units in each OEGMA monomer according to the M_n of the monomer).

Regarding reversibility of the phase separation, BzMA/MMA/VBK terpolymers exhibited irreversible phase separation below F_{MMA} = 18 mol% (B70/M20/V10-40). B60/M30/V10-40 with F_{MMA} = 22 mol% showed partial reversibility where the light transmittance of its solution increased up to about 60% after cooling; the phase separation of B50/M40/V10-40 with F_{MMA} = 29 mol% was observed to be completely reversed (ie. the light transmittance was restored to 100% after cooling).

By comparison, for BzMA/OEGMA/VBK terpolymers, the phase separation of B87/O3/V10-40 (F_{OEGMA} = 2 mol% or $F_{EG\ units}$ = 15 mol%) was totally irreversible. Complete reversal of phase separation was observed for both B8505V10-40 (F_{OEGMA} = 3 mol% or $F_{EG\ units}$ = 21 mol%) and B83/O7/V10-40 (F_{OEGMA} = 5 mol% or $F_{EG\ units}$ = 31 mol%). Hysteresis, or the difference between phase separation temperature and re-dissolution temperature, defined as the temperatures where light transmittance was measured to be 50% during heating and cooling, respectively, decreased from 25 °C for B85/05/V10-40 to 13 °C for B83/O7/V10-40. These results indicated that the reversibility of the phase separation for BzMA-rich terpolymers with a highly solvatophobic constituent (VBK) can be restored by incorporating sufficient amount of solvatophilic group (threshold between about 20 – 30 mol% of solvatophilic structure (ie. ester group in MMA or EG units in OEGMA) for both types of terpolymers).

One cannot however explain the restoration of reversibility of phase separation without understanding the mechanism of solvation. The dissolution of PBzMA in the IL was a result of the organization of the [NTf$_2$] anions around the equatorial position of the benzene plane of BzMA units and the imidazolium cation above and below the benzene ring's plane,[17] leading to a negative entropic term during mixing. As temperature rose, the increased kinetic energy of the ions led to liberation of the ions from the polymer, which resulted in phase separation. The potential π–π interactions between the benzyl group of BzMA units as well as those between BzMA and aromatic groups of VBK in the collapsed state can highly restrict the diffusion of IL ions to the polymers and render re-dissolution of the polymer impossible. A similar explanation is presented for PNIPAM (one of the most widely studied thermo-responsive polymer in aqueous solution), where the intramolecular hydrogen bonding in the globule state of PNIPAM act as "cross-linkers" and slowed re-dissolution.[50,51]

In this case, the statistically distributed solvatophilic groups throughout the terpolymer chains served as "separators" to increase the distance and reduce interactions between like BzMA units and between BzMA and VBK units, therefore making the polymer aggregate less compact and more available for IL diffusion during cooling.[49]

Kodama et al. reported that the rate of re-dissolution of PBzMA and its derivatives in various imidazolium-based ILs could be roughly correlated to the difference between polymer T_g and CPT of each polymer/IL system, ie. (CPT – T_g).[16] The correlation was attributed to an established empirical relation between polymer relaxation time and (T–T_g).[16,40] This is plausible since when CPT – T_g >> zero, the polymer chains were flexible when the re-dissolution process started, which can accelerate mutual diffusion between polymer chains and solvent during re-dissolution. For BzMA/OEGMA/VBK terpolymers, complete re-dissolution was observed when (CPT – T_g) increased from -1 to 20 °C and T_g of the terpolymers decreased from 70 to 64 °C. For the BzMA/MMA/VBK terpolymers, the phase separation became reversible when (CPT – T_g) increased from -6 to 6 °C even though T_g of the terpolymers increased from 85 to 89 °C. It appeared that the T_g of the polymer alone was not crucial for re-dissolution to occur, but the polymer needed to be sufficiently solvatophilic so that its CPT had to be higher than its T_g to undergo reversible phase separation.

3.2.2 Effects of solution concentration on transition temperature and reversibility

To investigate the effects of solution concentration on phase separation temperature and reversibility, a BzMA/MMA/VBK terpolymer (B60/M30/V10-40) and a BzMA/OEGMA/VBK terpolymer (B85/O5/V10-40) were dissolved in $[C_2mim][NTf_2]$ at concentrations varying from 1 to 10 wt%. The light transmittance of these solutions at varying temperature is shown in Figure 6. These two specific terpolymers were chosen because their phase separation reversibility was only partially restored at 3 wt% concentration (B60/M30/V10-40 solution showed light transmittance up to 60% during cooling; B85/O5/V10-40 phase separation was completely reversed with a large hysteresis of 25 °C). Therefore, the effects of solution concentration on the re-dissolution properties were likely the most apparent.

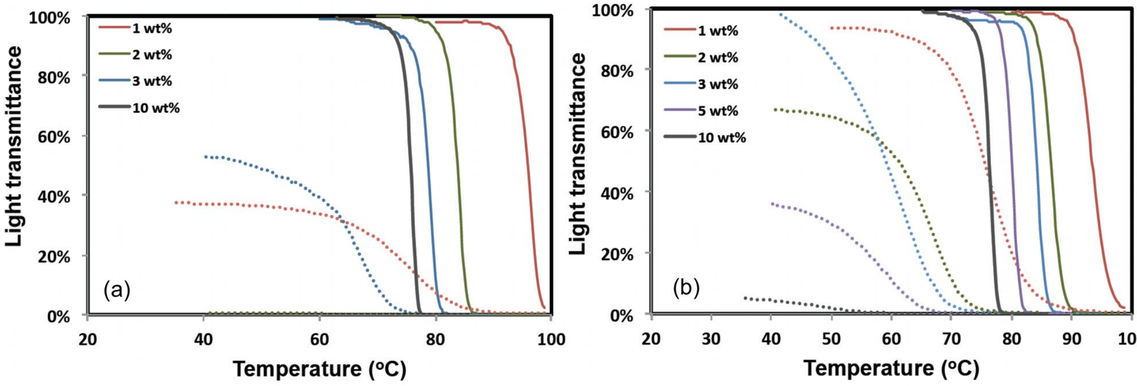

Figure 6: Light transmittance of 3 wt% terpolymer in ionic liquid solutions of (a) B60/M30/V10-40 (F_{BzMA} = 60 mol%, F_{MMA} = 22 mol%, F_{VBK} = 18 mol%), and (b) B85/O5/V10-40 (F_{BzMA} = 86 mol%, F_{OEGMA} = 3 mol%, F_{VBK} = 11 mol%) at various solution concentrations (heating cycles with solid lines and cooling cycles with dotted lines).

From Figure 6, the most noticeable effect of solution concentration for these two terpolymers was the decreasing CPT with increasing solution concentration. For both terpolymers, CPT decreased by about 20 ºC as concentration increased from 1 to 10 wt% (96 to 75 ºC for B60/M3/0V10-40 and 93 to 76 ºC for B85/O5/V10-40). This general trend of decreasing CPT with increasing solution concentration was consistent with other polymers with LCSTs in both aqueous[52,53] and IL[13] solutions.

It should be noted that there are some differences in the concentration effect between aqueous and IL solutions. In aqueous solutions, the transition temperature is usually only sensitive to concentration in dilute solutions (typically below ~ 1 wt%)[29,52,54,55] By comparison, in IL solutions, the transition temperature remained sensitive to concentration changes at higher concentrations. In this study, the CPT of the terpolymer solutions decreased continuously with increasing concentration up to 10 wt%. Similarly, Lee et al. reported that the CPT of poly(n-butyl methacylate) solutions in an IL changed gradually by more than 40 ºC from 0.25 to 5 wt%.[13] Since thermo-responsive polymers were sensitive to a wider range of concentrations in ILs and the change in transition temperature can be substantial, solution concentration can be a very useful tool to fine tune LCST in IL solutions.

For reversibility, it was observed that with lower polymer concentration, a higher degree of re-dissolution, indicated by higher light transmittance after cooling, could be generally achieved. At 10 wt%, both terpolymers showed completely irreversible phase separation. Below 10 wt%, various degrees of reversibility were observed. For B60/M30/V10-40, its solutions at 1 wt% and 3 wt% showed about 40% and 60% light transmittance after cooling, respectively, whereas the solution at 2 wt% exhibited irreversible phase separation. For B85/O5/V10-40, its solution at 1, 2, 3, and 5 wt% showed maximum light transmittance of about 95%, 65%, 100%, 40% after cooling, respectively. Replicates of the 2 and 3 wt% solutions showed that the results of both CPT and light transmittance after cooling were reproducible. Thus, although it is more intuitive to assume polymer in more dilute solution would re-dissolve more readily after phase separation, solution concentration did not correlate strongly with the extent of re-dissolution in the range of 1 – 5 wt%.

3.2.3 Effects of molecular weight on transition temperature and reversibility

The effects of number average molecular weight ($\bar{M}_n$) on transition temperature and reversibility were illustrated using BzMA/MMA/VBK terpolymers of similar composition (F_{BzMA} ~ 75 mol%, F_{MMA} ~ 10 mol%, F_{VBK} ~ 15 mol%) at three different $\bar{M}_n$s (7.3, 13.6, 22.5 kg mol^{-1}) in Figure 7. These terpolymers were synthesized with the same feed composition (80 mol% BzMA, 10 mol% MMA and 10 mol% VBK, noted as B80/M10/V10-15, B80/M10/V10-40, B80/M10/V10-80 in Table 4) and the LCST behavior of B80/M10/V10-40 was already demonstrated in Figure 4. This particular composition was used because CPT could not be obtained for terpolymers with higher MMA content at low $\bar{M}_n$~ 7 kg mol^{-1} (ie. no phase separation up to the instrument upper limit, 100 °C).

As $\bar{M}_n$ increased from 7.3 to 22.5 kg mol^{-1}, CPT decreased significantly from 84 to 55 °C. This trend of decreasing CPT with increasing $\bar{M}_n$ is consistent with other thermo-responsive polymers in ILs.[13,14] The inverse dependency of LCST in aqueous solutions on molecular weight was also well documented.[56-58] Zhu et al.[57] demonstrated experimentally that the contribution to the entropy of mixing decreased significantly with increasing chain length, which makes dissolution more difficult, or in other words, favors phase separation. It was also shown by Patterson[58] that LCST is proportional to the critical value of the Flory-Huggins interaction parameter (χ_c), which can be correlated to the ratio of molar volume of polymer to that of the solvent (*r*):

Equation 1

$$\chi_c = \frac{(1 + {}^{1}\!/\!\sqrt{r})^2}{2}$$

Using Equation 1, LCST decreases when *r* increases. As the molar volume of polymer is proportional to polymer chain length, it is clear that LCST has to decrease with increasing molecular weight.

Regarding phase separation reversibility, all three terpolymers cited above showed irreversible phase separation. The value of (CPT – T_g) of each polymer/IL system was used earlier to represent the flexibility of the polymer chains at the start of re-dissolution process and the larger the value, the faster the mutual diffusion between polymer chains and IL ions and hence the re-dissolution process. Interestingly, the value of (CPT- T_g) of B80/M10/V10-15 (F_{MMA} = 9 mol%) was 17 ºC, which was larger than the (CPT – T_g) of 6 ºC for B50/M40/V10-40 (F_{MMA} = 29 mol%). However, B80/M10/V10-15 showed irreversible phase separation while the phase separation for B50/M40/V10-40 was reversible. Therefore, one should be careful that the value of (CPT – T_g) may be used to correlate to re-dissolution kinetics, but it cannot be used as an indicator for whether re-dissolution would occur or not. Since the only difference between the two terpolymers besides $\overline{M}_n$ (and hence T_g) was their compositions, these results illustrated that although $\overline{M}_n$ and T_g played important roles in the CPT of the terpolymers, sufficiently high concentration of solvatophilic groups in the terpolymer was necessary to drive the re-dissolution process.

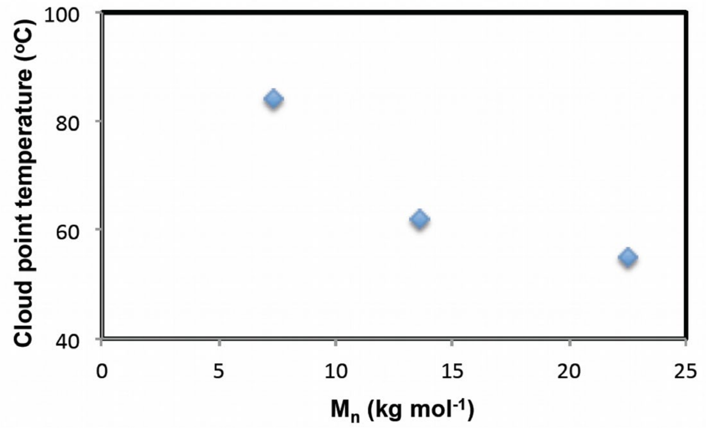

Figure 7: Cloud point temperature of 3 wt% solutions in [C_2mim][NTf_2] of B80/M10/V10-10 (F_{BzMA} = 75 mol%, F_{MMA} = 9 mol%, F_{VBK} = 16 mol%), B80/M10/V10-40 (F_{BzMA} = 74 mol%, F_{MMA} = 10 mol%, F_{VBK} = 16 mol%), and B80/M10/V10-80 (F_{BzMA} = 77 mol%, F_{MMA} = 9 mol%, F_{VBK} = 14 mol%) versus M_n relative to PMMA standards.

3.2.4 Reversibility of the phase separation and terpolymer fluorescent properties

After discovering incorporating a sufficient amount of solvatophilic co-monomer could restore phase separation reversibility, verification of the reversibility under repeated heating and cooling was studied. IL solutions of B50/M40/V10-40 (F_{BzMA} = 51 mol%, F_{MMA} = 29 mol%, F_{VBK} = 20 mol%) and B83/O7/V10-40 (F_{BzMA} = 81 mol%, F_{OEGMA} = 5 mol% (eq. $F_{EG\ units}$ = 31 mol%), F_{VBK} = 14 mol%) were heated above their CPT and then cooled to room temperature four times consecutively while the solution light transmittance was monitored. As shown in Figure 8, all heat/cool cycles appeared to be very similar. Slightly faster re-dissolution was observed during the first cooling compared to the consequent cycles for both terpolymers. Nonetheless, hysteresis stayed relatively constant with +/- 1 °C variance during all the cycles for both terpolymers. Therefore, we concluded that the phase separation reversibility of both terpolymers was predictable and consistent for at least 4 heat/cool cycles.

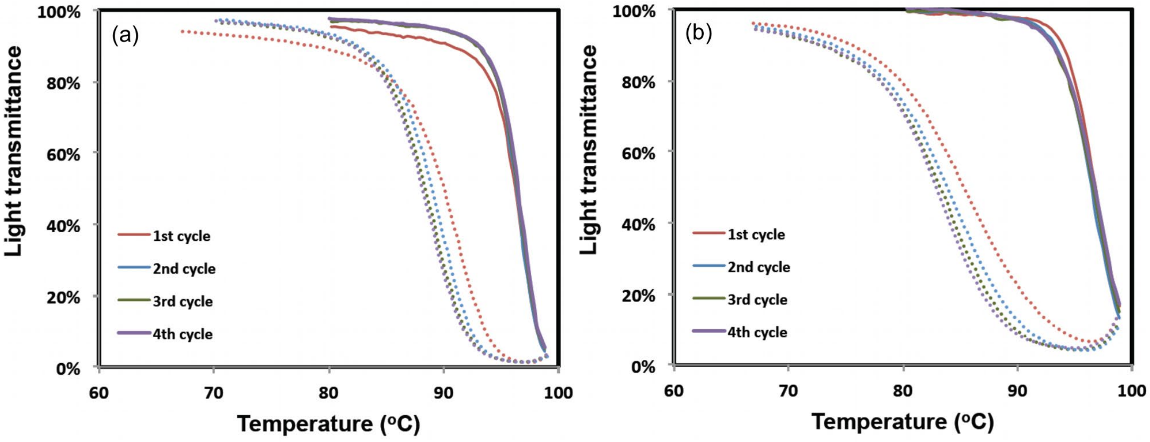

Figure 8: Light transmittance of (a) B50/M4/0M10-40 (F_{BzMA} = 51 mol%, F_{MMA} = 29 mol%, F_{VBK} = 20 mol%) and (b) B83/O7/V10-40 (F_{BzMA} = 81 mol%, F_{OEGMA} = 5 mol%, F_{VBK} = 14 mol%) in 3 wt% [C_2mim][NTf_2] solutions during 4 consecutive heat/cool cycles (solid line represents heating and dotted line represent cooling).

In our previous study,[27] an interesting fluorescence phenomena was observed for BzMA/VBK random copolymers in [C_2mim][NTf_2] where the fluorescence intensity of the solution increased sharply as the copolymer phase separated from the IL. It was attributed to the enhanced fluorescence resonance energy transfer (FRET) efficiency between BzMA and VBK after phase separation because of its strong dependency on the donor/acceptor distance.[27,60] Since phase separation reversibility could be restored, fluorescence enhancement triggered by the phase separation was expected to be reversible as well. Therefore, the fluorescence intensity of B50/M40/V10-40 and B83/O7/V10-40 in [C$_2$mim][NTf$_2$] was measured while the solution was heated and cooled for 3 consecutive cycles (Figure 9).

For B50/M40/V10-40, the maximum fluorescence intensity remained relatively constant as the solution was heated until the CPT of 95 °C, after which the intensity increased rapidly by about 2-fold. For B83/O7/V10-40, similar fluorescence enhancement at its CPT was observed to be about 5-fold during the first heating cycle and about 3-fold during the two consequent cycles. In the previous study of BzMA/VBK copolymers, the enhancement was observed to be about 5-fold.[27] The decrease in enhancement for the terpolymers can be a result of the collisions between BzMA or VBK and MMA or OEGMA units, causing non-radiative relaxation.[61]

It was also noted that the fluorescence behavior of the terpolymers was different during the first cycle compared to the two consequent cycles. The terpolymers were dissolved in the IL at temperature below their T_gs. Therefore, internal stresses may develop while the glassy polymer chains were changing their conformation in the viscous solutions.[62,63] These stresses can be relaxed after the first heating, resulting in different polymer chain conformations and consequently different fluorescence properties for subsequent cycles.

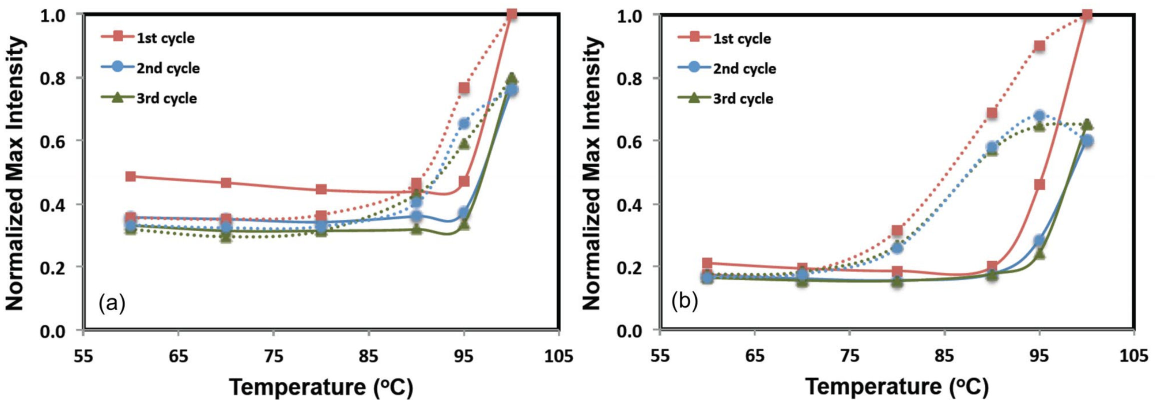

Figure 9: Normalized maximum fluorescence intensity (excitation at 330 nm) of (a) B50/M40/M10-40 (F_{BzMA} = 51 mol%, F_{MMA} = 29 mol%, F_{VBK} = 20 mol%) and (b) B83/O7/V10-40 (F_{BzMA} = 80 mol%, F_{OEGMA} = 8 mol%, F_{VBK} = 12 mol%) in 3 wt% [C_2mim][NTf_2] solutions during 3 consecutive heat/cool cycles (solid line represents heating and dotted line represent cooling).

Lastly, the reduction in fluorescence intensity during cooling was observed to be more gradual than the enhancement during heating for all cycles. The hysteresis in fluorescence response can be explained by the much more rapid process of aggregation than re-dissolution for both terpolymer systems studied.[35] The slow swelling process of the aggregates during cooling led to a gradual increase in distance between BzMA and VBK. Consequently, the FRET efficiency did not decrease as sharply during cooling as when it increased during phase separation. Thus, the fluorescence enhancement was confirmed to be essentially reversible and relatively consistent during the 3 consecutive heat/cool cycles for both of the selected BzMA/MMA/VBK and BzMA/OEGMA/VBK terpolymers.

4. CONCLUSIONS

Terpolymers of BzMA/MMA/VBK and BzMA/OEGMA/VBK were synthesized via NMP with fixed $f_{VBK,0}$ = 10 mol% and varying BzMA/MMA ($f_{BzMA,0}$:$f_{MMA,0}$ = 80:10 to 50:40) or BzMA/OEGMA ($f_{BzMA,0}$:$f_{OEGMA,0}$ = 87:3 to 80:10) compositions at 90 ºC in a controlled manner.

The concentration of solvatophilic groups (ie. ester group in MMA and EG units in OEGMA) was illustrated to be the dominant factor affecting solubility and the extent of re-dissolution of the terpolymers in [C_2mim][NTf_2]. A minimum of 20 – 30 mol% solvatophilic groups was found necessary to facilitate complete re-dissolution for both terpolymer systems. Both increasing solution concentration and molecular weight resulted in decreased CPT. However, the solution concentration correlated weakly with the extent of re-dissolution and irreversible phase separation was observed for the lowest M_n (7.3 kg mol^{-1}) investigated.

Finally, the phase separation reversibility of the two terpolymer systems was demonstrated to be consistent and predictable for at least 4 consecutive heat/cool cycles. The fluorescence response was also shown to be reversible and relatively consistent within 3 heat/cool cycles.

In summary, the incorporation of the solvatophilic content in the terpolymer with BzMA and VBK was successful in facilitating and accelerating the re-dissolution process of the terpolymer after its LCST phase separation in the IL. We showed that the solvatophilicity can be quantified and tuned by adjusting the composition of solvatophilic groups in the terpolymers. To our knowledge, this is the first time the effects of solvatophilicity of polymers on the LCST phase separation and reversibility in IL solutions were studied quantitatively. The encouraging results represented an important step towards the development of robust and reusable fluorescence-based temperature sensitive devices based on polymer/IL solutions.

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