

# Polymerization-Induced Phase Separations in Branched Poly(methyl methacrylate) Synthesis

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**ABSTRACT:** Methyl methacrylate and ethylene glycol dimethacrylate or 1,6-hexanediol dimethacrylate (HDDMA) were copolymerized in the presence of a nonsolvent (heptane) for poly(methyl methacrylate) (PMMA) to examine the phenomenon of polymerization-induced phase separations (PIPS) in branched PMMA synthesis. The process was dependent upon the amount of nonsolvent and crosslinker in the reaction mixture. Gel particles were obtained in the majority of phase-separated systems, and their formation was promoted by the preferential partition of monomer and

crosslinker into the precipitated polymer phase during the phase separation process. Experimental data showed that, because of its lower solubility parameter, HDDMA can be used as crosslinker to minimize gel particle formation in systems where PIPS is present. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1462–1468, 2005

**Key words:** poly(methyl methacrylate); crosslinking; free-radical polymerization; phase separation; gels

## INTRODUCTION

Although free-radical copolymerization of mono-vinyl monomers and multi-vinyl crosslinkers is predominantly used for the preparation of macroscopic polymer networks, it can also be used to produce various soluble branched polymers.<sup>1</sup> Generally, the branched polymers resulting from these polymerizations have high molecular weights and relatively low viscosities in a range of solvents. They have been used as binders or coating materials<sup>2,3</sup> and as drug or enzyme carriers.<sup>4</sup>

The methodology for the preparation of soluble branched polymers entails the prevention of macrogelation in the polymerizations. It is well known in the synthesis of polymer networks that macrogelation of copolymerization mixtures is promoted by high total monomer or crosslinker concentrations<sup>5</sup> and increased chain lengths of the primary polymer molecules.<sup>6</sup> (The term primary polymer molecule describes the imaginary linear polymer that would exist if all the crosslinks connected to it were severed.<sup>7,8</sup>) Therefore, soluble branched polymers have been obtained at low total monomer or crosslinker contents<sup>9,10</sup> or by adding various chain transfer agents to the reaction mixtures.<sup>11,12</sup>

During our investigations on the effects of polymerization solvents on hydrogel synthesis,<sup>13,14</sup> in which

free-radical copolymerizations of various water-soluble monomers [acrylamide and *N,N'*-methylenebisacrylamide or 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate (EGDMA)] were conducted in the presence of various nonsolvents for the polymers, we observed the formation of insoluble polymer particles prior to their macrogelations. This partial gelation of the reaction mixture was also observed when we attempted to prepare branched poly(methyl methacrylate) (PMMA) by copolymerizing MMA and EGDMA in mixed-solvent systems where phase separation can occur. The formation of these gel particles is distinctively different from macrogelations, but it is still highly undesirable because it reduces product yield and makes steady-state operations impossible in industrial production.

The origins of polymerization-induced phase separation (PIPS) and gel particle formation in MMA copolymerizations were studied and a means to avoid this phenomenon is proposed. Mixtures of *p*-xylene (good solvent for PMMA) and heptane (nonsolvent for PMMA) were used as polymerization solvents in order to examine the effects of polymer–solvent compatibility. EGDMA and 1,6-hexanediol DMA (HDDMA) were used as crosslinkers to investigate the effects of crosslinker solubility on the gel formation process.

## EXPERIMENTAL

### Materials

MMA (99%), EGDMA (98%), HDDMA, azobisisobutyronitrile (AIBN), heptane (99+%), *p*-xylene (99+%),

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and basic aluminum oxide were obtained from Aldrich Chemicals (Castle Hill, Australia). Methanol and tetrahydrofuran (THF, HPLC grade) were obtained from Ajax FineChem (Seven Hills, Australia), and *d*-chloroform [1% tetramethyl silane (TMS)] was obtained from Cambridge Isotope Laboratories (Andover, MA).

MMA, EGDMA, and HDDMA were filtered through an activated basic alumina column, distilled under reduced pressure, and stored at 4°C. AIBN was recrystallized from ethanol. Unless specified, all other reagents were analytical grade and used without further purification.

The monomer solutions are classified according to their monomer content (weight percent of total monomers in the reaction mixture) and crosslinker content (mole percent of crosslinker in the monomer mixture). The *p*-xylene and heptane concentrations of the reaction mixtures are given in weight percentages.

### Measurements

Size exclusion chromatography (SEC) measurements in THF were carried out using a Waters 510 HPLC pump equipped with three Phenomenex phenogel columns (500, 10<sup>4</sup>, and 10<sup>6</sup> Å) in series with a Wyatt Dawn F laser photometer operating at 90° and in parallel with a Waters 410 differential refractometer [refractive index (RI)] and a Viscotek T50A differential viscometer. Data acquisition and analysis were performed with Viscotek TriSEC software. Calibration of all three detectors was achieved using PMMA standards.

The <sup>1</sup>H-NMR spectra were measured on a 400-MHz Unity spectrometer using *d*-chloroform as the solvent and TMS as a reference. Monomer conversions of the reaction mixture were determined from the integration ratio of the methoxy carbon peaks of MMA ( $\delta$  3.95) and PMMA ( $\delta$  3.8).

### Typical procedure for preparation of branched PMMA in *p*-xylene

In a typical preparation of PMMA with 10 wt % monomers and 2 mol % crosslinker, a mixture of MMA (1.92 g, 19.2 mmol), EGDMA (0.078 g, 0.39 mmol), AIBN (0.01 mol %/monomer, 32 mg), and *p*-xylene (18 g) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze-pump-thaw cycles and then heated at 80°C for 20 h. At the end of the reaction, a sample was taken from the reaction mixture and analyzed directly by SEC and <sup>1</sup>H-NMR. The reaction mixture was finally precipitated into methanol (2 L).

### Typical procedure for preparation of branched PMMA in mixtures of *p*-xylene and heptane

In a typical preparation of PMMA with 10 wt % monomers and 2 mol % crosslinker in the presence of 20% heptane, a mixture of MMA (1.92 g, 19.2 mmol), EGDMA (0.078 g, 0.39 mmol), AIBN (0.01 mol %/monomer, 32 mg), *p*-xylene (14 g), and heptane (4 g) was added to a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by three freeze-pump-thaw cycles and then heated at 80°C for 20 h. At the end of the reaction, THF (10 g) was added to the reaction mixture to dissolve the precipitated branched polymers and a sample was taken from the reaction mixture and analyzed directly by SEC. The mixture was then filtered to remove the gel particles and the filtrate was precipitated into methanol (2 L). Then, the gel particles were dried in a 120°C oven for 1 week to determine the gel yield of the reaction.

## RESULTS AND DISCUSSION

The free-radical copolymerization of mono-vinyl monomers and multi-vinyl crosslinkers in solution leads to the formation of various branched polymers, which increase in molecular weight as the reaction proceeds.<sup>15,16</sup> In this work soluble branched PMMA is synthesized in various mixtures of *p*-xylene and heptane to examine the effects of the solvent and the phase separation on the polymerization.

### Free-radical copolymerization of MMA and EGDMA

In the first set of experiments, MMA and EGDMA were copolymerized at various total monomer and crosslinker concentrations to examine the effects of these reaction parameters, and *p*-xylene was used as the polymerization solvent in order to avoid phase separations. The weight-average molecular weight ( $M_w$ ) and polydispersity (PD) of the resulting soluble polymers and the monomer conversions of the systems are provided in Table I.

At 10 wt % monomers, soluble polymers are formed at all crosslinker concentrations. The  $M_w$  and PD of the resultant polymers both increased with increasing amounts of crosslinkers in the reaction mixture. Although the increases in the  $M_w$  are consistent with the increasing number of potential crosslinks in the system, increases in the PD can be attributed to the enhanced autoacceleration effect,<sup>17-19</sup> which is associated with the decreased termination rates at intermediate to high monomer conversions of the polymerizations that produced polymers with high molecular weights. The very high  $M_w$  and PD with 8 mol % EGDMA indicate that the reaction mixture is near its gel point.<sup>10</sup>

TABLE I  
Molecular Weight and Polydispersity of PMMA Formed with Various Weight Percentages of Monomers and Mole Percentages of Crosslinker

Monomers (wt %)	Crosslinker (mol %)	<i>p</i> -Xylene	$M_w$	$M_w/M_n$	Monomer conversion (%)	Appearance
10	0	90	13,000	1.4	91	Solution
10	2	90	69,700	3.6	90	Solution
10	4	90	1,960,000	6.2	88.4	Solution
10	8	90	200,000,000	80.5	80.6	Solution
20	2	80	2,824,000	24.0	85.1	Solution
20	4	80	—	—	—	Gel
20	8	80	—	—	—	Gel
30	2	70	—	—	—	Gel
40	2	60	—	—	—	Gel

Macrogelation of the reaction mixtures was observed when the monomer concentration was increased from 10 to 20 wt % at 4 mol % EGDMA or to 30 wt % at 2 mol % EGDMA. According to the classical gelation theory by Flory,<sup>7</sup> macrogelation occurs when the dimension of the polymeric network approaches that of the reaction vessel. Therefore, the observed gelations at high monomer concentrations can be understood in terms of their increased polymer volumes. In contrast, the different thresholds of total monomer concentration obtained at various crosslinker concentrations is consistent with results obtained from the soluble polymer systems, which show that increases in the percentage of crosslinker lead to an increase in the  $M_w$  of the polymer mixture.

In this work, MMA polymerizations with 10 wt % monomers and 2 mol % crosslinker were chosen as the model system in the following studies of phase separations because they produced PMMAs with molecular weights of typical soluble branched polymers [number-average molecular weight ( $M_n$ ) of 10,000–40,000, according to refs. 10 and 20] and high monomer conversions.

### Effects of heptane on MMA/EGDMA systems

Miscibility in a multicomponent system is governed by its Gibbs free energy of mixing ( $\Delta G_{\text{mix}}$ ), which is a function of the enthalpies of mixing ( $\Delta H_{\text{mix}}$ ) and the entropies of mixing ( $\Delta S_{\text{mix}}$ ) between the various components in the mixture ( $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$ ). When MMA and a multi-vinyl crosslinker are copolymerized in the presence of a nonsolvent, the  $\Delta S_{\text{mix}}$  of the reaction mixtures is expected to decrease with increasing monomer conversion because of the increased polymer content of the system and increases in the polymer molecular weight caused by crosslinking reactions. Because the  $\Delta H_{\text{mix}}$  between PMMA and the nonsolvent is positive, PIPS can occur at a critical monomer conversion, which is determined by the de-

creasing  $\Delta S_{\text{mix}}$  of the system, and the relative rates of the polymerization and phase separation process.

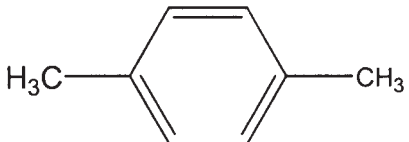
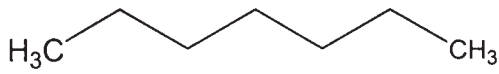
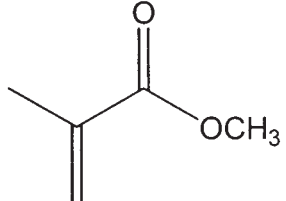
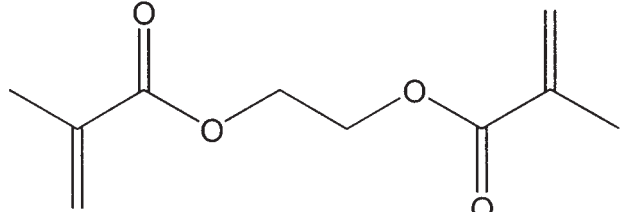
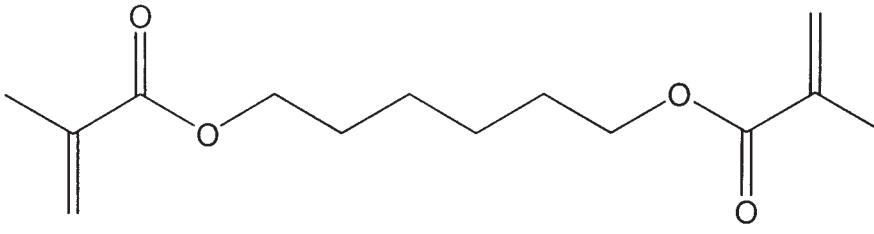
In order to examine the phenomenon of phase separation and gel particle formation, mixtures of MMA and EGDMA (10 wt % monomers, 2 mol % crosslinker) were copolymerized in various mixtures of *p*-xylene and heptane. Heptane was chosen as the nonsolvent for PMMA because it has low compatibility with PMMA,<sup>21</sup> which is reflected by their significantly different solubility parameters ( $\delta$ , Table II).

At >10% heptane, the initially clear reaction mixture became slightly opalescent and the formation of gel particles was simultaneously observed. The amount of gel particles in the reaction mixture was increased with increasing heptane concentrations whereas the amount of soluble polymer was decreased. The  $M_w$  and PD of the soluble polymers and the fraction of PMMA in the soluble polymer phase and the gel phase are shown in Table III.

The effect of the heptane concentration on the molecular weight of the soluble polymers was dependent on the phase behavior of the reaction mixture. In the absence of phase separation (<10% heptane), the  $M_w$  increases with increasing heptane concentrations. Conversely, it decreased with increasing heptane concentrations in the phase-separated systems.

The molecular weight distribution (MWD) of the soluble polymers obtained in the phase-separated system is further illustrated in Figure 1, which shows the SEC chromatograms of the polymers. The PD of the polymers decreased with increasing heptane concentrations. Interestingly, although similar MWDs were obtained at the low molecular weight end of the chromatogram (high retention volumes), the high molecular weight end of the RI traces was shifted to higher retention volumes as the heptane content of the reaction mixture was increased. This reveals that one of the effects of the formation of gel particles in the reaction mixture is to remove a significant portion of polymers with high molecular weights from the reac-

TABLE II  
Solubility Parameters of Various Solvents and Monomers

	Solubility parameters (MPa <sup>0.5</sup> )	Chemical structure
Poly(methyl methacrylate) <sup>25</sup>	18.6	
<i>p</i> -Xylene <sup>25</sup>	18.8	
Heptane <sup>25</sup>	15.1	
Methyl methacrylate <sup>25</sup>	18.0	
Ethylene glycol dimethacrylate <sup>26</sup>	18.6	
1,6-Hexanediol dimethacrylate <sup>26</sup>	14.8	

tion mixture, such that the final  $M_w$  of the remaining soluble polymers is decreased. As the heptane concentration in the reaction mixture is increased, the  $M_w$  and yield of soluble polymers are decreased because the gel fraction of the reaction mixture is increased.

In our previous work,<sup>6</sup> we observed that the polymerization solvent can affect the structures of polymer networks by influencing the chain lengths of the first formed polymers in the reaction mixture; it was expected that heptane would have a similar effect on the PMMA system. To examine the changes in the molecular weights obtained at low heptane concentrations, 10 wt % MMA was homopolymerized (in the absence of crosslinker) with various heptane-*p*-xylene mixtures (Fig. 2).

The homopolymerizations were homogeneous at low heptane concentrations and became opalescent at 15% heptane. However, because of the absence of crosslinker in the reaction mixture, the formation of

gel particles was not observed in the phase-separated systems and, after the polymerization, the precipitated polymers were redissolved into the bulk soluble polymer phase prior to the SEC analysis.

Although no crosslinker was present in the reaction mixture, the  $M_w$  of the linear polymers increased with increasing heptane concentration of the reaction mixture. The occurrence of phase separations can therefore be attributed to both the increased  $\Delta H_{\text{mix}}$  (caused by the increasing amount of nonsolvent) and the decreased  $\Delta S_{\text{mix}}$  (caused by the increased  $M_w$  of PMMA) in the system. The molecular weight increases are consistent with the reported reductions in the termination rates of MMA polymerizations when poor solvents of PMMA were used as polymerization solvents<sup>22,23</sup> and with results obtained from the copolymerization system. It shows that one of the dominant effects of introducing heptane in MMA homo- or copolymerizations is

**TABLE III**  
Molecular Weight and Polydispersity of PMMA (10 wt % monomers, 2 mol % EGDMA) Synthesized in Various Heptane-*p*-Xylene Mixtures

Heptane (wt %)	<i>p</i> -Xylene (wt %)	$M_w$	$M_w/M_n$	Recovered Product (%)		
				Branched polymer	Gel	Appearance
0	90	69,700	3.6	100	0	Clear solution
5	85	78,300	4.1	100	0	Clear solution
7.5	82.5	87,900	4.3	100	0	Clear solution
10	80	143,800 <sup>a</sup>	4.9 <sup>a</sup>	87	13	Opalescent solution with gel particles
12.5	77.5	74,500 <sup>a</sup>	2.5 <sup>a</sup>	77	23	Opalescent solution with gel particles
15	75	35,500 <sup>a</sup>	1.5 <sup>a</sup>	70	30	Opalescent solution with gel particles
20	70	33,100 <sup>a</sup>	1.4 <sup>a</sup>	31	69	Opalescent solution with gel particles

<sup>a</sup> The data are based on all soluble polymers in the reaction mixture.

to increase the chain lengths of the primary polymer molecules.

In contrast to the homopolymerization systems, we observed that phase separation in MMA and EGDMA copolymerizations eventually leads to the formation of insoluble gel particles in the reaction mixtures. This can be explained in terms of the partitioning of monomers into the two different phases that are formed during the phase separation process: the soluble polymer phase (phase I) and the precipitated polymer phase (phase II).

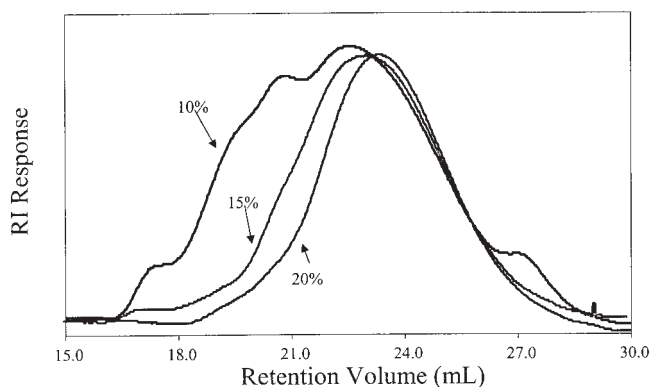
At the onset of the phase separation process, all the components of the reaction mixture (MMA, EGDMA, PMMA, heptane, and *p*-xylene) are partitioned into the two new phases, the relative concentrations in each phase being dependent upon their solubility parameters. Phase II of the final reaction mixture is expected to have a higher  $\delta$  value than that of phase I because (as evident from the gelation of phase II) it has higher PMMA and lower heptane concentrations. As a

result, the formation of gel particles in the reaction mixtures can be attributed to the preferential partitions of MMA and EGDMA into phase II (driven by their similar  $\delta$  values with PMMA), which increases both the total monomer and crosslinker concentrations of phase II such that they are higher than those of phase I, and of the reaction mixture prior to the phase separation process.

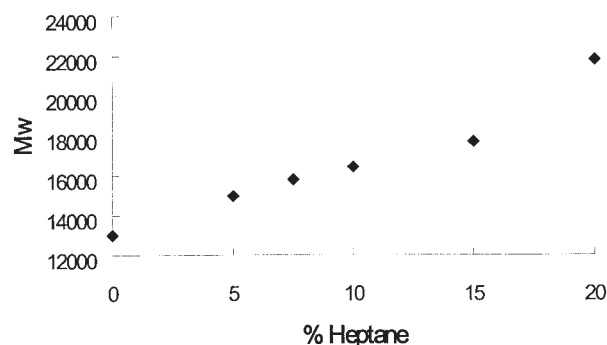
#### Effects of heptane on MMA/HDDMA systems

The divinyl monomer HDDMA has a significantly lower  $\delta$  than PMMA and is therefore used as crosslinker in the reaction mixtures. In contrast to EGDMA, HDDMA is expected to be preferentially partitioned into phase I during the phase separation process and therefore will reduce the amount of gel particle formation in the phase-separated mixtures.

Mixtures of MMA and HDDMA (10 wt % monomers, 2 mol % crosslinker) were copolymerized in various *p*-xylene-heptane mixtures, and the  $M_w$  and



**Figure 1** An SEC trace (RI detector) of PMMA (10 wt % monomers, 2 mol % EGDMA) synthesized in the presence of 10, 15, and 20% heptane.



**Figure 2** The weight-average molecular weight data of linear PMMA synthesized in the presence of various amounts of heptane.



TABLE IV  
Molecular Weight and Polydispersity of PMMA (10 wt % Monomers, 2 mol % HDDMA) Synthesized in Various Heptane-*p*-Xylene Mixtures

Heptane (wt %)	<i>p</i> -Xylene (wt %)	$M_w$	$M_w/M_n$	Recovered product (%)		Appearance
				Branched polymer	Gel	
0	90	22,400	1.2	100	0	Clear solution
5	85	37,000	1.4	100	0	Clear solution
7.5	82.5	46,400	2.6	100	0	Clear solution
10	80	53,600	2.3	100	0	Opalescent solution with precipitated polymer
11.25	78.75	47,000	1.7	100	0	Opalescent solution with precipitated polymer
12.5	77.5	56,900	2.1	100	0	Opalescent solution with precipitated polymer
13.75	76.25	86,200	2.8	100	0	Opalescent solution with precipitated polymer
15	75	89,200 <sup>a</sup>	5.8 <sup>a</sup>	85	15	Opalescent solution with gel particles
20	70	25,740 <sup>a</sup>	1.5 <sup>a</sup>	63	27	Opalescent solution with gel particles

<sup>a</sup> The data are based on all soluble polymers in the reaction mixture.

PD of the resultant soluble branched polymers were determined (Table IV). Phase separation of the reaction mixture was observed at 10% heptane; however, the formation of gel particles was not observed until 15% heptane was used. The obtained gel fractions of the phase-separated mixtures were significantly lower than the corresponding EGDMA system. Between 10 and 15% heptane, the precipitated polymers were redissolved with the bulk soluble polymers prior to the SEC analysis.

It is well known that the thermodynamics of polymer systems are dictated by the  $M_n$  and volume fraction of the macromolecules.<sup>24</sup> The molecular weight data show that phase separation occurred in the 10% heptane reaction mixture when the  $M_n$  of the polymer was around 20,000, which is consistent with results obtained for the EGDMA series and indicates that HDDMA has crosslinking efficiency comparable to EGDMA.

The effect of the heptane concentration on the molecular weight of the soluble polymers, which were prepared using HDDMA as the crosslinker, was again observed to be dependent upon the phase behavior of the reaction mixture. In the absence of phase separation (<10% heptane), the  $M_w$  and PD of the branched PMMA were increased with increasing heptane concentrations, which can be attributed to the increased chain lengths of the primary PMMA molecules in reaction mixtures that have high heptane contents. In contrast, the significant reductions in the  $M_w$  when the heptane content of the reaction mixture was increased from 15 to 20% can be explained in terms of the formation of gel particles in the reaction mixture.

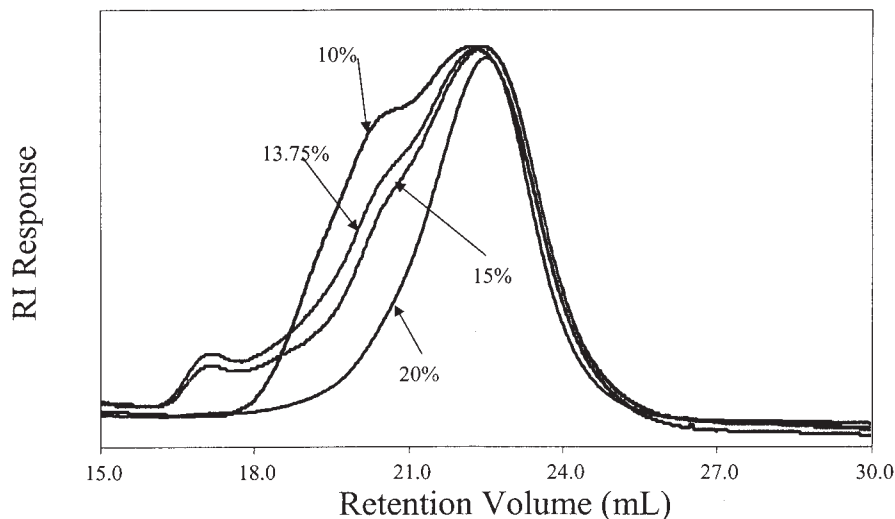
Despite the occurrence of phase separation between 10 and 15% heptane, no gel particles were obtained in the reaction mixture and all the precipitated polymers became soluble as more solvents were added to the reaction mixture. This is consistent with the reduced  $\delta$  value of the crosslinker, which reduces the amount of HDDMA in phase II and therefore prevents the formation of gel particles.

Figure 3 shows the MWDs of soluble polymers obtained with 10, 13.75, 15, and 20% heptane. Note that the chromatograms are distinctly different from those with 13.75 and 15% heptane; they are multimodal, and two distinct peaks (at high molecular weight and low molecular weight) are observed. This reveals the presence of very high molecular weight species in the reaction mixture, which is probably the branched PMMA in the precipitated polymer phase. The high molecular weight peak was not observed at lower heptane concentrations because of the reduced extent of phase separation in the reaction mixture. However, at 20% heptane, the phase-separated phase has undergone gelation and therefore does not constitute as soluble polymers.

## CONCLUSION

This work examined the effects of PIPS on the preparation of soluble branched PMMA. The phase separation process was found to be dependent upon the amount of heptane and crosslinker in the reaction mixture.

In the copolymerizations of MMA and EGDMA, the phenomenon of gel particle formation was observed



**Figure 3** An SEC trace (RI detector) of PMMA (10 wt % monomers, 2 mol % HDDMA) synthesized in the presence of 10, 13.75, 15, and 20% heptane.

in all of the phase-separated mixtures. This can be largely ascribed to the preferential partition of monomeric MMA and EGDMA into the precipitated polymer phase of the reaction mixture, which increases its total monomer and crosslinker concentrations. The partition of the crosslinker was found to be dependent on its  $\delta$  value and promoted by crosslinkers with similar  $\delta$  values with PMMA. HDDMA was used to demonstrate how the formation of gel particles can be avoided in phase-separated PMMA systems.

The effects of the heptane concentration on the molecular weight of the resultant soluble branched polymers were observed to be dependent upon the phase behavior of the reaction mixture. In the absence of PIPS, the  $M_w$  increased with increasing heptane concentrations because of the increased chain lengths of the primary PMMA molecules in the reaction mixture. In the phase-separated systems where gel particle formation was absent, polymers with multimodal MWDs were obtained and two distinct peaks were evident from the SEC chromatogram of the polymer. Finally, in the phase-separated systems in which gel particle formation was also observed, the  $M_w$  and PD decreased with increasing heptane concentrations because the polymers with high molecular weights were removed from the mixture via gelation.

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