

Crosslinked Methyl Methacrylate/Ethylene Glycol Dimethacrylate Polymer Compounds with a Macroazoinitiator

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ABSTRACT: A silane-containing diamine, bis(*p*-aminophenoxy) diphenylsilane (BADPS), was prepared by the condensation of *p*-aminophenol with dichlorodiphenyl silane in the presence of triethylamine. Then, BADPS was condensed with 4,4-azobis(4-cyanopentanoyl chloride) to prepare macroazoinitiators containing silane units (Si-MAIs). A series of poly(methyl methacrylate) gels containing silane were derived by the solution free-radical crosslinking copolymerization of methyl methacrylate and

ethylene glycol dimethacrylate monomers initiated by these macroazoinitiators at a total monomer concentration of 6 mol/L and 80°C. Si-MAIs were characterized with ¹H-NMR and ¹³C-NMR spectroscopy, and the structural characteristics of the gels were also examined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 382–393, 2010

Key words: crosslinking; gelation; gels; polysiloxanes; silicones

INTRODUCTION

The use of polymeric initiators, such as macroazoinitiators (MAIs), with labile azo groups is a well-known method for preparing various block copolymers by conventional radical polymerization.^{1–14} Synthesis with MAIs provides some advantages. Not only are block copolymers composed of addition polymer segments, but also those of addition polymers and various oligomer segments can be synthesized with MAIs in radical processes. In addition, MAIs enable researchers to combine different kinds of polymerization reactions, where MAIs can be prepared by the use of materials with both polycondensation¹⁵ or polyaddition functionality^{16,17} and a thermally labile azo linkage as radical initiation species.¹⁸ However, it is an important factor to synthesize an MAI containing one or more azo groups in the main chain for the molecular structure of block copolymers. Depending on the type of MAI and termination reaction, diblock (AB), triblock (ABA), or multiblock [(AB)_{*n*}] copolymers can be obtained. Many studies have focused on the preparation of different block copolymers with different types of MAIs by heating in the presence of a vinyl monomer.^{19,20} The incorporation of silicone segments into common vinyl polymers would lead to an

interesting group of thermoplastic elastomers with low glass-transition temperatures, high lubricity, high gas permeability, and so on. In recent years, many studies have been reported with MAIs containing silicone segments for the synthesis of silicone–vinyl block copolymers.^{21–29} The MAI prepared by the condensation of 4,4-azobis(4-cyanopentanoyl chloride) (ACPC) and α,ω -bis(3-aminopropyl)dimethyl polysiloxanes in equimolar amounts was found to be a useful candidate for the radical polymerization of vinyl monomers with a typical product of poly(dimethylsiloxane-*b*-methyl methacrylate) (PDMS-*b*-PMMA).²¹ Inoue et al.²¹ showed that the incorporation of the polydimethylsiloxane (PDMS) segment in the block copolymers improved the thermal stability of polystyrene (PSt). Hamurcu et al.²³ reported the production of block and graft copolymers such as poly(dimethylsiloxane-*b*-styrene) (PDMS-*b*-PSt) and poly(dimethylsiloxane-*g*-butadiene) with NH₂-terminated PDMS-based MAIs obtained by the reaction of ACPC with an α,ω -amine terminated PDMS prepolymer. It was also reported that crosslinked block copolymers of styrene containing PDMS units could be prepared with a macroinimer with PDMS units, and the thermal properties of crosslinked PDMS-*b*-PSt copolymers were compared with the copolymers of styrene prepared by PDMS MAIs.²⁴ Chang et al.²⁵ studied the synthesis and thermodecomposition kinetics of hydroxybutyl-terminated MAIs (PDMS-ACP) with various molecular weights and prepared PDMS-*b*-PMMA copolymers with PDMS-ACP MAIs. The activation

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energy, activation enthalpy, and activation entropy of the thermodecomposition of PDMS-ACP in toluene increased with increasing PDMS chain length (SCL) in the PDMS moieties, whereas the activation free energy was independent of the SCL. In another study, Chang et al.²⁶ prepared PDMS-*b*-PSt copolymers with PDMS-ACP MAIs, investigated the thermal and thermooxidative degradation of these copolymers, and found that the incorporation of PDMS segments in the block copolymers improved the thermooxidative stability of PSt. The aim of this study was the synthesis of crosslinked poly(methyl methacrylate) (PMMA) based on bis(*p*-aminophenoxy) diphenylsilane (BADPS) with different concentrations of an MAI containing silane units (Si-MAI) with an ethyl methyl ketone (EMK)/dichloromethane (DCM) solvent mixture (3 : 1 molar ratio) as the reaction medium. The indicated EMK/DCM solvent mixture was used to dissolve Si-MAI completely so that a homogeneous reaction medium was obtained. First, the synthesis of Si-MAI based on ACPC and BADPS was performed in one stage. Then various initial amounts of Si-MAI were used to initiate the radical polymerizations of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) in solution. The main contribution of this study was the use of Si-MAI for the synthesis of silicone-containing PMMA gels and the resulting copolymer networks with better properties by the determination of the optimum polymerization conditions and the evaluation of the physical properties of the gels.

EXPERIMENTAL

Materials and equipment

4,4-Azobis(4-cyanopentanoic acid) (ACPA) was used as received from Fluka AG. ACPA was converted to an acid chloride derivative ACPC with a melting point of 97°C. *p*-Aminophenol (PAP) and dichlorodiphenyl silane (DCDPS) were purchased from Merck Chemical Co. (Darmstadt, Germany) and were used without further purification. MMA and EGDM were purchased from Acros (Janssen Pharmaceutical, Geel, Belgium). The monomers were freed of inhibitor by washing in a 5% aqueous NaOH solution and distilled water and drying over anhydrous Na₂SO₄. The initiator, 2,2-azobis(2-methyl propionitrile) (AIBN; Merck), was recrystallized three times from absolute methanol, followed by drying in a vacuum oven at room temperature. Methanol, toluene, benzene, petroleum ether, chloroform, hexane, EMK (LabScan, Dublin, Ireland), triethylamine (TEA; J. T. Baker, Phillipsburg, NJ), and DCM (LabScan) were used as dried and purified in the conventional manner. Fourier transform infrared (FTIR) spectroscopy analysis was performed with a Nicolet Impact 400 D

model spectrophotometer (Nicolet Impact, Madison, WI) with KBr pellets. The spectra were obtained over the wave-number range 4000–500 cm⁻¹ at a resolution of 2 cm⁻¹ with a mercury cadmium telluride detector with the coaddition of 64 scans. Scanning electron microscopy (SEM) micrographs were taken on a JEOL-JXA 840 A scanning electron microscope (JEOL, Boston, MA). The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen, and the application of a gold coating of approximately 300 Å with an Edwards S 150 B sputter coater.

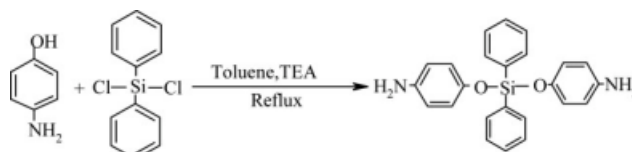
Monomer synthesis

Preparation of BADPS (Scheme 1)

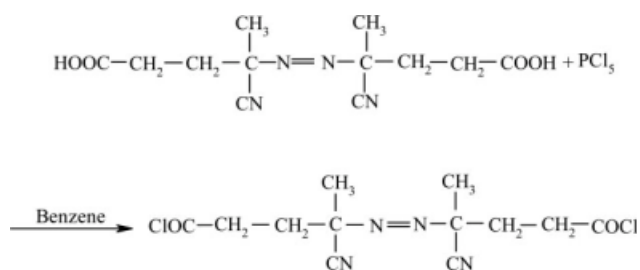
DCDPS (6.45 mL, 50 mmol) was added dropwise to a well-stirred slurry mixture of PAP (10.92 g, 100 mmol), anhydrous TEA (15.26 g, excess 10%), and 200 mL of fresh distilled toluene at -5°C in a 500-mL, three-necked flask that was dried, purged with nitrogen, and fitted with a mechanical stirrer and a condenser. After the addition, the mixture was then heated to a gentle reflux and was continuously stirred for 24 h. The color of the slushy mixture was slightly yellow at first, and then, it gradually turned brown. When its color turned deep brown, the mixture was cooled to room temperature. The white byproduct triethylhydroammonium chloride salt was filtered off quickly to minimize contamination of the product by hydrolysis when the salt was exposed to moisture. The viscous crude product (10.42 g) was recovered after removal of the solvent with an evaporator. The crude product was then dissolved in chloroform and filtered. The solvent of the filtrate was removed, and the residue was finally dried in a vacuum at 50°C. The final product was a viscous brown oil (yield = 6.32 g, 60%).

Synthesis of ACPC (Scheme 2)

PCl₅ (4.2 g, 20 mmol) was added to 60 mL of dry benzene, which included 20 mmol of ACPA, and the resulting solution was stirred for 3 h at room temperature. The solvent was extracted *in vacuo*, and the product was dissolved in dry chloroform. This solution was precipitated in petroleum ether; the product was washed with a mixture of *n*-hexane/



Scheme 1 Preparation of BADPS.



Scheme 2 Preparation of ACPC.

petroleum ether (1 : 3 molar ratio) for further purification. The yield of reaction was 75 %.

Preparation of Si-MAIs

The low-temperature solution polycondensation method was applied for the synthesis of silane-based MAIs with a scissile azo group in the main chain. The reaction for the synthesis of Si-MAI is shown in Scheme 3.

Si-MAI was prepared as follows. A solution of 20 mmol ACPC in 50 mL of chloroform was added to a mixture of 40 mmol of BADPS prepolymer and 30 mL of aqueous NaOH (10% w/w), and the solution was stirred for 24 h at room temperature. The molar ratio of ACPC to BADPS was 1 : 2. Then, the solution was washed with water three times to secure the removal of the salts and ACPA from the product. The organic phase was dried with sodium sulfate overnight at 0°C, and the solvent was evaporated. The viscous liquid was dried *in vacuo* and stored at 0°C until use.

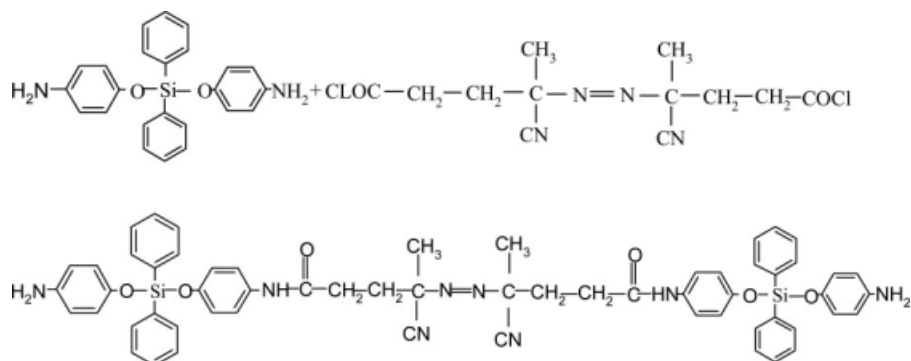
Polymerization procedure

We prepared monomer solutions shortly before use by weighing the required amounts of MMA, EGDM, EMK/DCM, and Si-MAI. Pyrex ampules with a 10 mm internal diameter and a length of about 70 mm were each filled with 2 g of monomer solution. After they were degassed with four successive

freeze-thaw cycles with liquid nitrogen and a reduced pressure of 1.3 KPa, the ampules were torch sealed. The polymerization was initiated by immersion of the ampules in an oil bath maintained at a constant temperature of $80 \pm 0.1^\circ\text{C}$, and we quenched the reaction by thrusting the ampules into liquid nitrogen. We assumed that the surface-to-volume ratio of the ampules was high enough to assure isothermal conditions. A typical recipe for the preparation of silicone-containing PMMA gels and the process are given in Table I and Scheme 1, respectively. The homologous series of polymer gels prepared in this way allowed systematic variation of the EMK/DCM, MMA, EGDM, and Si-MAI concentrations. The copolymer samples for conversion measurements were obtained by a gravimetric technique. For this purpose, the monomers and solvent mixture were pipetted into a 100-mL, three-necked, round-bottom flask containing a Teflon-coated magnetic stirring bar, and the appropriate amount of Si-MAI was then added. To eliminate oxygen from the system, nitrogen was bubbled through the reaction mixture at room temperature for 30 min. Then, the reactor was placed in a thermostated bath at 80°C . To detect the end of the induction period, usually a few minutes, small samples were removed from the reactor by means of a syringe and added to methanol. The time of the first appearance of a stable white color was recorded as $t = 0$. Then, samples were taken at various reaction times via syringes, and they were precipitated dropwise into an agitated solution of methanol. We determined the conversion of monomer by drying and weighing the precipitated polymer. The gel point was determined experimentally as the midpoint between the last time at which a soluble polymer was obtained and the point at which the mixture was not soluble in EMK/DCM (Scheme 4).

Extraction of the sol fraction

EMK/DCM was chosen as the extraction solvent mixture and was used at room temperature. The



Scheme 3 Preparation of Si-MAI.

TABLE I
Polymerization Recipe

Run	Si-MAI (mol/L)	MMA (mol/L)	EGDM (mol/L)
1	3.20×10^{-3}	4.60	1.470
2	4.20×10^{-3}	4.60	1.470
3	4.70×10^{-3}	4.60	1.470
4	6.63×10^{-3}	4.60	1.470
5	1.32×10^{-3}	4.60	1.470
6	1.99×10^{-3}	4.60	1.470
7	3.31×10^{-3}	4.60	1.470
8	4.64×10^{-3}	4.60	1.470

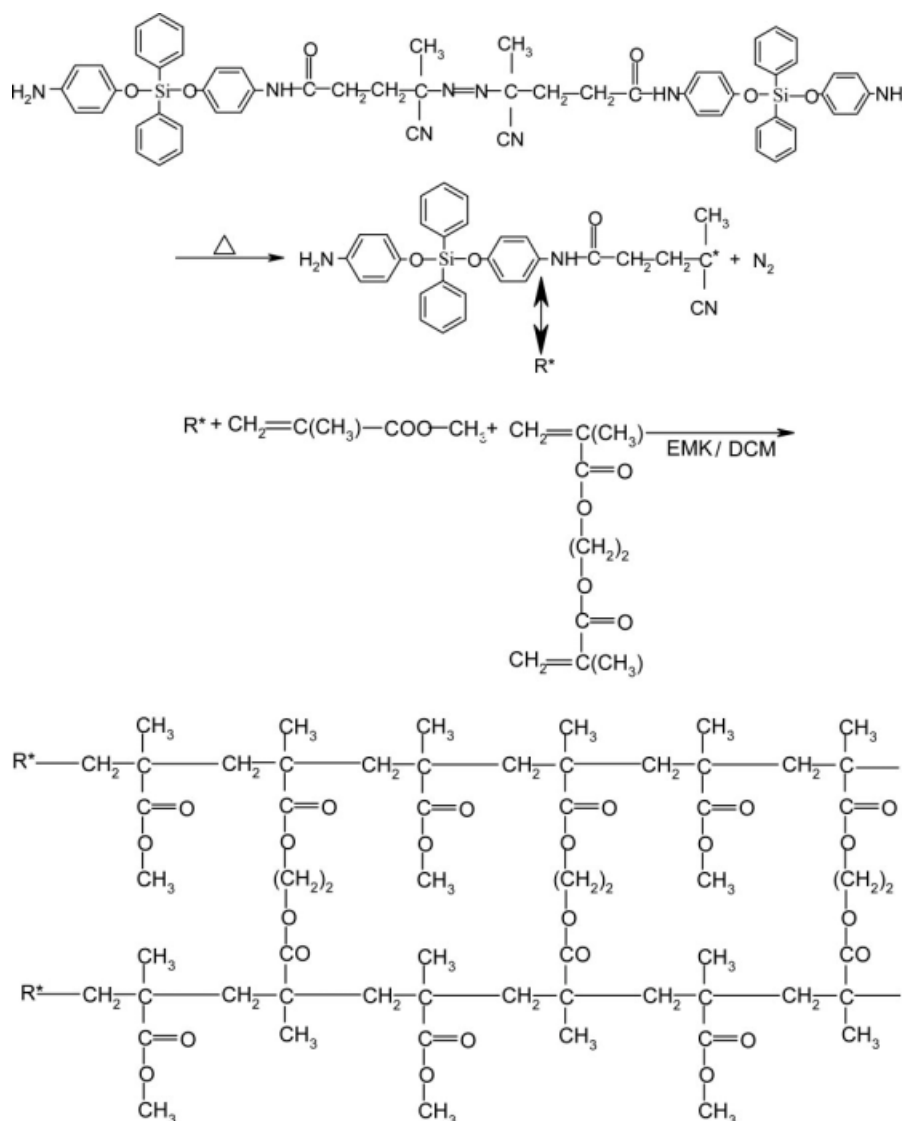
Initial monomer concentration = 6 mol/L; temperature = 80°C; solvent = EMK/DCM.

crude gels, 10 mm in diameter, were cut into samples 10–25 mm in length. Each sample was placed in an excess of EMK/DCM containing a small amount

of 1,4-benzoquinone as an inhibitor, and the solvent was replaced every other day over a period of 3 weeks until no further extractable polymer could be detected. The networks after extraction were carefully deswollen in a series of (EMK/DCM)/methanol mixtures with increasing methanol content. They were then washed several times with methanol and dried at room temperature *in vacuo* to a constant weight. The amount of soluble polymer in the EMK/DCM solution was determined gravimetrically after evaporation and precipitation in methanol. The weight fraction of the gel (W_g) was calculated as follows:

$$W_g = \frac{g}{g + s} \quad (1)$$

where g and s are the weights of the extracted network and soluble polymer, respectively.



Scheme 4

Swelling measurements

The swelling measurements were carried out in EMK/DCM at room temperature. To determine the equilibrium degree of swelling, the networks were immersed in EMK/DCM for at least 3 weeks, and we tested the swelling equilibrium by weighing the samples. To achieve higher precision, three measurements were carried out on samples of different weights taken from the same gel. The networks were then weighed in the swollen state and dried, after a solvent exchange with methanol as described previously, *in vacuo* to a constant weight. The extent of swelling was characterized by the equilibrium volume swelling ratio in EMK/DCM (q_v):

$$q_v = 1 + \frac{(q_w - 1)\rho_p}{\rho_s} \quad (2)$$

where q_w is the ratio of the weights of the gel in the swollen state and the dry state and ρ_p and ρ_s are the densities of the polymer and solvent, respectively.

RESULTS AND DISCUSSION

The structures of the BADPS, Si-MAI, and PMMA copolymers before the gel point were confirmed through FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy and are shown in Figures 1–7, respectively. Figure 1(A–C) shows the FTIR spectra of DCDPS, PAP, and BADPS. The bands due to NH— bending for primary amines at 3340 and 3277 cm^{-1} and —C=O

stretching for amides at 1616 cm^{-1} , respectively, are characteristic absorptions of BADPS [Fig. 1(C)]. The characteristic bands due to Si—CH₃ at 840 and 1023 cm^{-1} and Si—O—Ph at 966 cm^{-1} of silicone units were assigned to BADPS. Figure 2 represents the $^1\text{H-NMR}$ spectra of BADPS, where the signals of the —CH₂ resonance (2.32–2.71 ppm) and the MAI protons (0.084 ppm) in siloxane segments were observed. Figure 3 indicates the $^{13}\text{C-NMR}$ spectrum of BADPS. The number of carbons in the BADPS was compatible with the number of spectra. Figure 4(A–D) illustrates the FTIR spectrum of ACPA, ACPC, BADPS, and Si-MAI, respectively. Comparison of the spectrum of ACPA with that of ACPC showed that the strength and wide peak of carboxylic acid was omitted at 2500–3500 cm^{-1} , which was related to conversion of ACPA to ACPC. Also, a comparison between the spectra of BADPS and Si-MAI showed a peak at 1661 cm^{-1} , which corresponded to —C=O stretching for amides. The characteristic peaks of Si-MAIs were observed at 3400 cm^{-1} for the —NH stretching vibration band, 1660 and 1522 cm^{-1} for carbonyl absorption, 1244 and 840 cm^{-1} for Si—CH₃ deformation, and 1093 cm^{-1} for Si—O—Si asymmetric stretching vibration. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of Si-MAI are shown in Figures 5 and 6. The expected structures of the Si-MAIs were confirmed by these figures and agreed well with the literature structures of similar compounds.^{21,23–25} The FTIR spectra of the PMMA copolymers before the gel point are shown in Figure 7(A,B) with AIBN and (Si-MAI), respectively. A

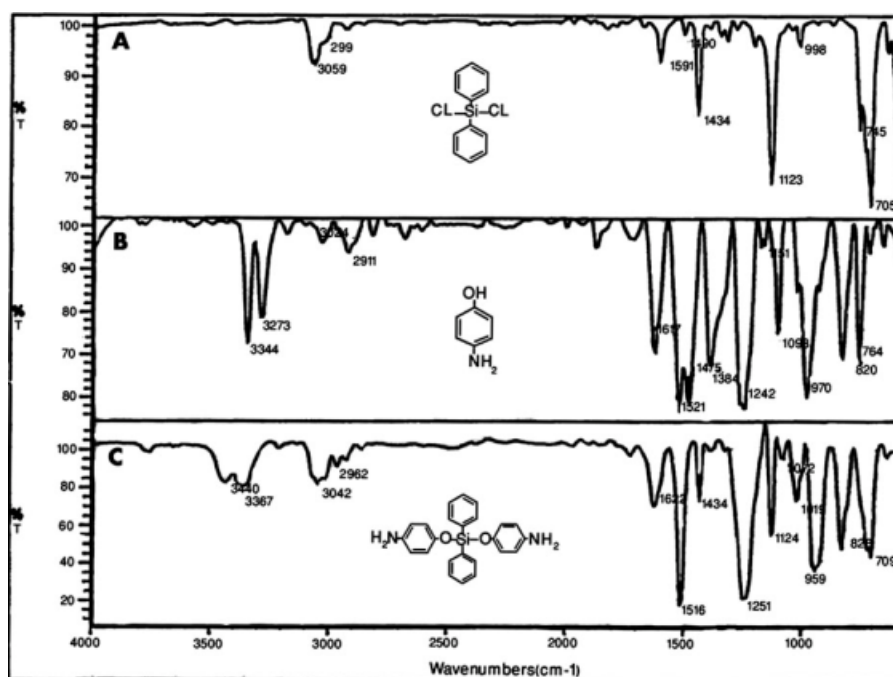


Figure 1 FTIR spectra of (A) DCDPS, (B) PAP, and (C) BADPS.

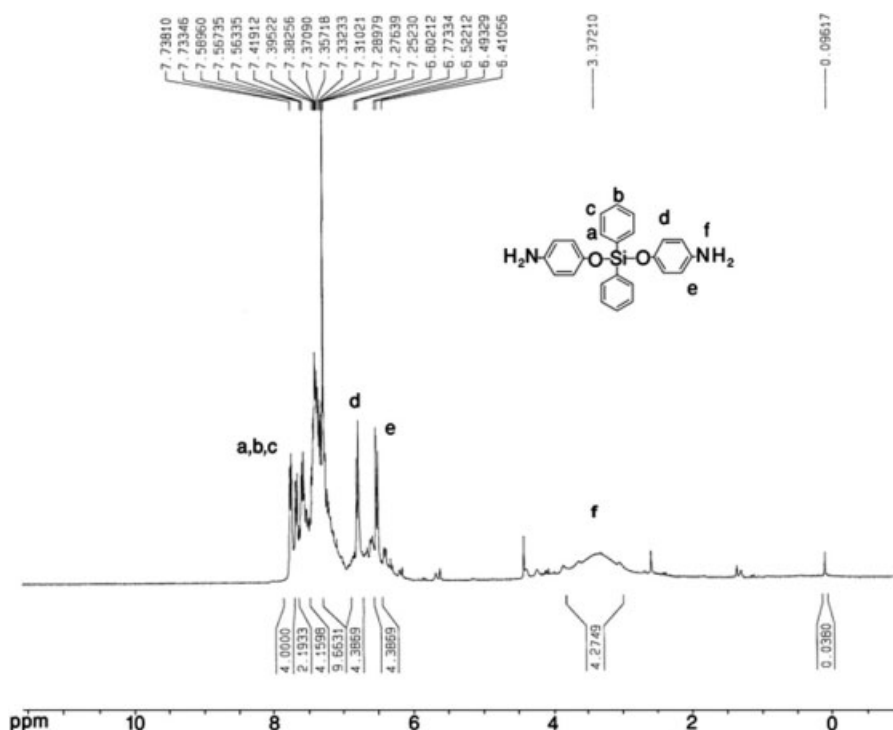


Figure 2 $^1\text{H-NMR}$ spectrum of BADPS.

comparison of the two spectra showed that the presence of peaks at 834 and 1255 cm^{-1} were related to the Si-CH_3 moiety, and the peaks at 3256 and 3389 cm^{-1} were related to the NH_2 , and a peak at 1662 cm^{-1} was related to the -C=O stretching for amides. All of the spectra in these figures exhibited clear and sharp peaks in the region of $3500\text{-}500\text{ cm}^{-1}$.

Effects of the Si-MAI concentration on the MMA/EGDM gel properties

Increasing the Si-MAI concentration resulted in a decrease in the both W_g and q_v (Fig. 8). Also, the conversion percentage showed a drastic increase, whereas the gel point showed a decrease (Fig. 9). It is well known that four types of reactions are

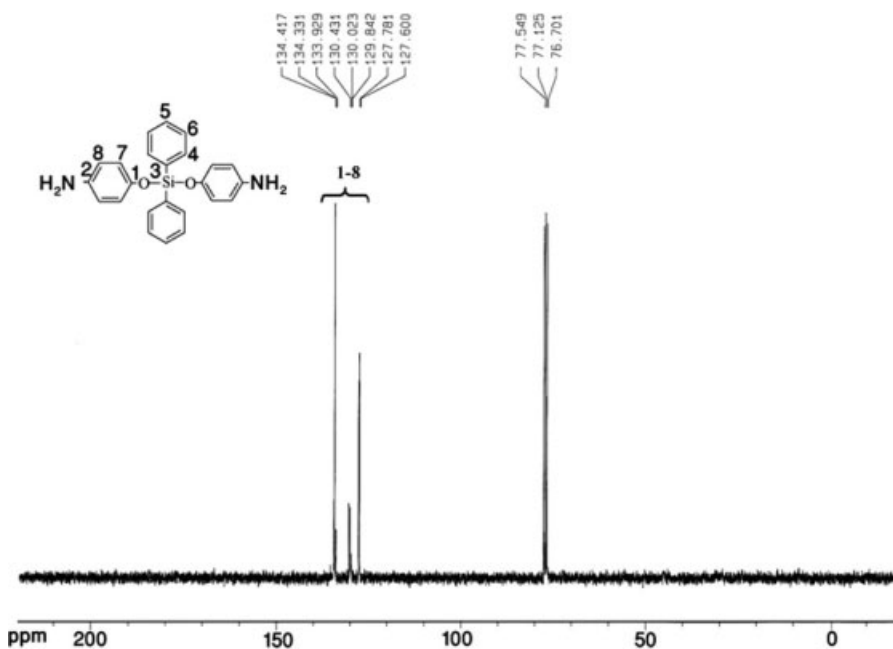


Figure 3 $^{13}\text{C-NMR}$ spectrum of BADPS.

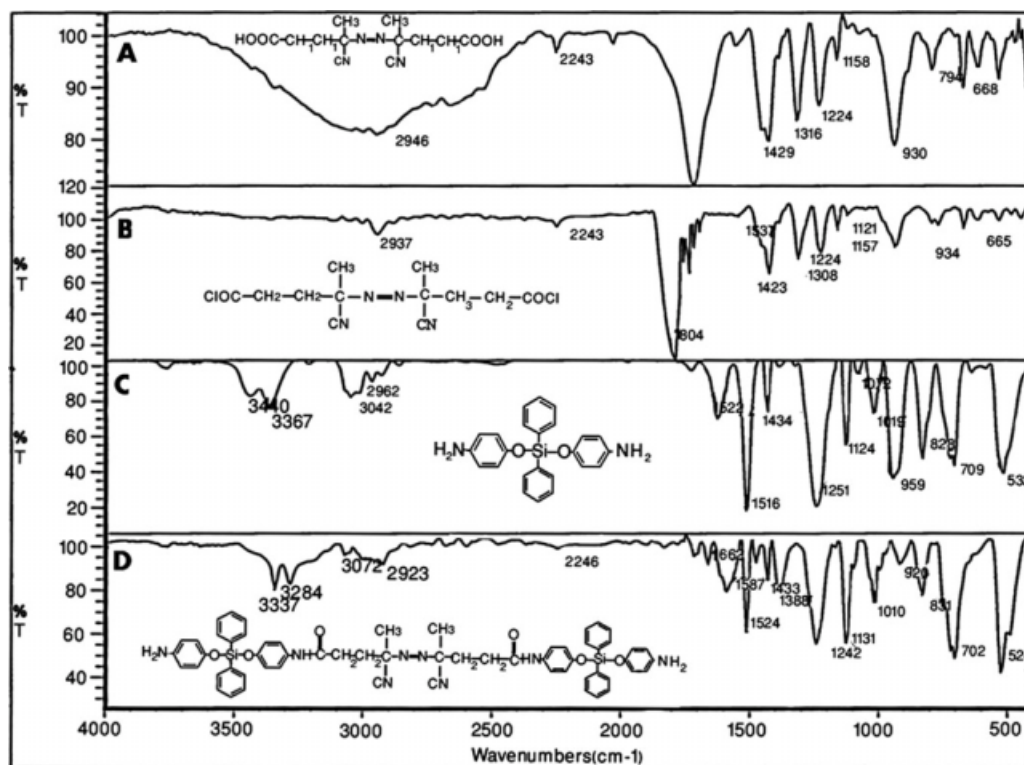


Figure 4 FTIR spectra of (A) ACPA, (B) ACPC, (C) BADPS, and (D) Si-MAI.

involved in free-radical polymerization, namely, initiation, propagation, termination, and chain transfer.³⁰ Also, the free-radical crosslinking copolymerization system involves three types of vinyl groups: those on vinyl and divinyl monomers and those on

polymer chains, that is, pendant vinyls.³¹ Accordingly, the polymerization system can be considered a special case of terpolymerization, in which one of the vinyl groups (pendant vinyls) is created during the course of the reaction when the vinyl on the

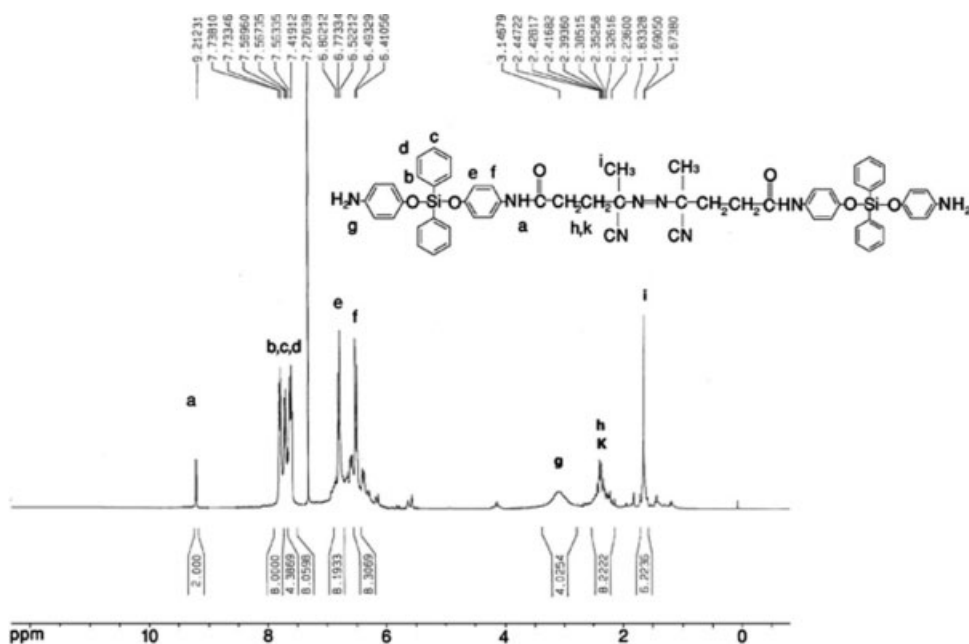


Figure 5 ¹H-NMR spectrum of Si-MAI.

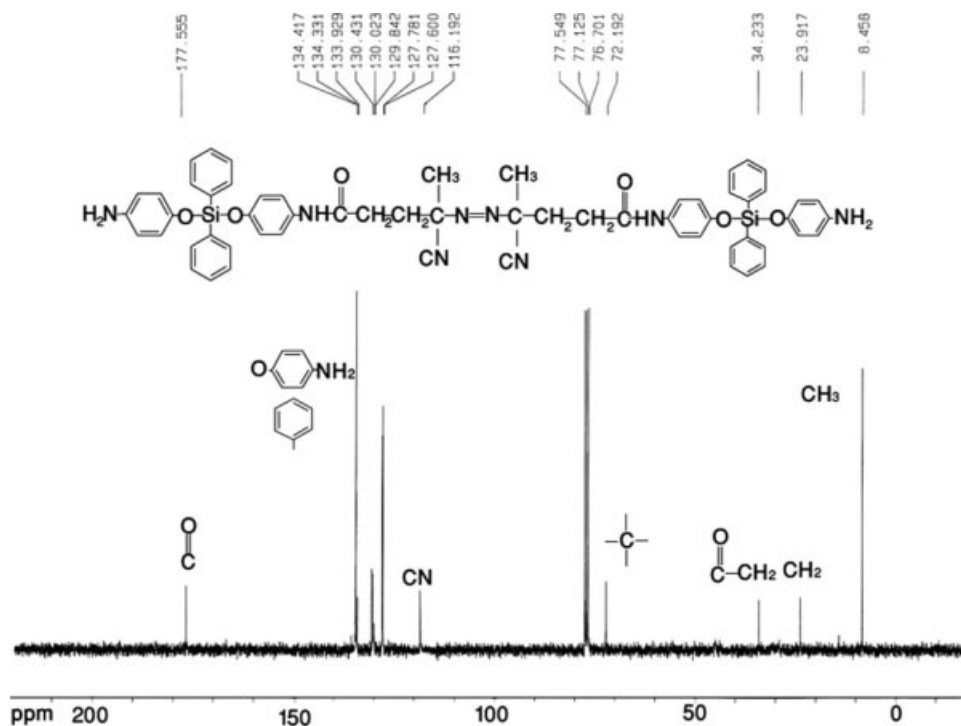


Figure 6 ^{13}C -NMR spectrum of Si-MAI.

divinyl monomer reacts. The formed pendant vinyl groups can then react by cyclization, crosslinking, or multiple crosslinking reactions or remain pendant.

With cyclization, a cycle is formed when the macro-radical attacks the pendant vinyl group in the same kinetic chain, whereas with multiple crosslinking, it

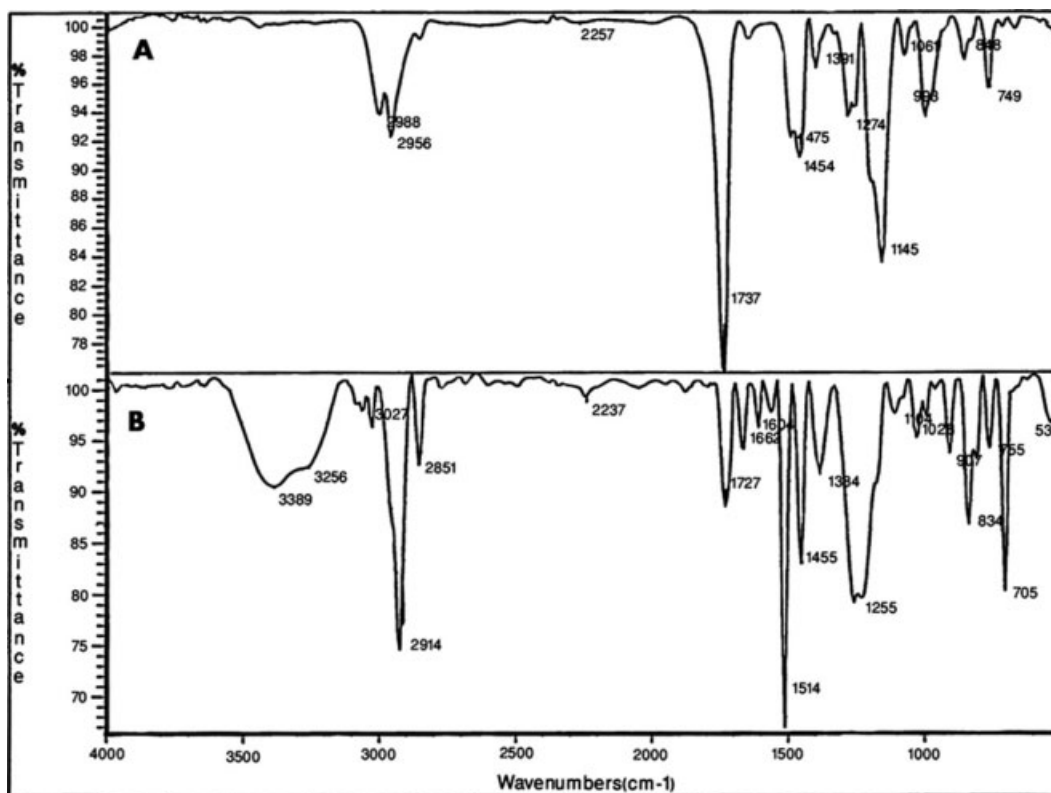


Figure 7 FTIR spectra of PMMA gels by (A) AIBN and (B) Si-MAI.

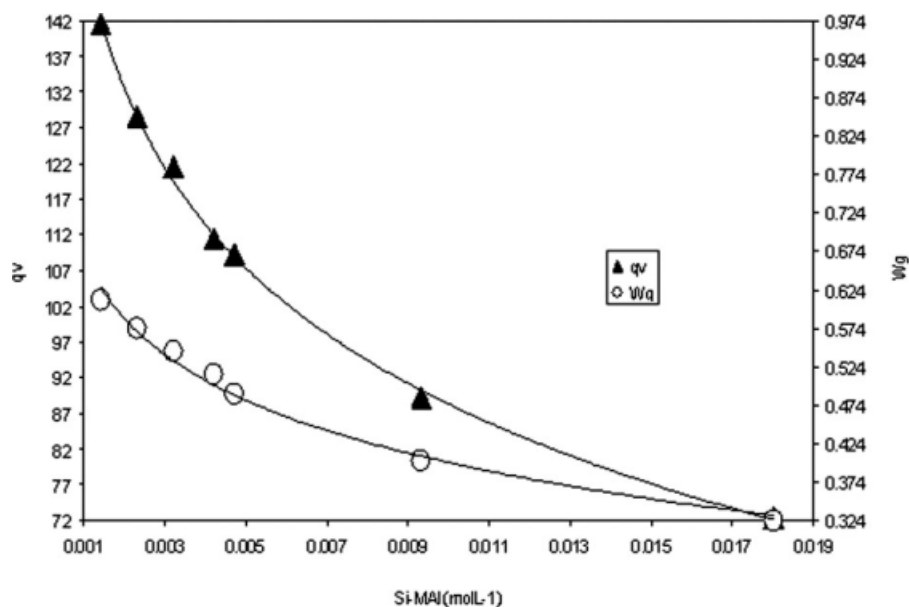


Figure 8 (○) W_g and (▲) q_v as functions of the Si-MAI concentration for MMA and EGDM copolymerization in EMK/DCM at 80°C (initial monomer concentration = 6 mol/L).

is formed if the radical attacks the pendant double bonds on other chains already chemically connected to the growing radical.^{32,33} Cyclization and multiple crosslinking have been redefined as primary and secondary cyclization, respectively.³⁴ On the other hand, when a three-dimensional network is formed, the reactive species chemically bound to the network, such as the pendant double bonds and free-radical centers, have extremely small diffusion coefficients, which can significantly suppress their reactivity; this is based on swelling measurement and

theoretical discussions, even to the extent that they may be considered to be trapped and unavailable for reactions. In this system, the EGDM crosslinker contained two double bonds, and according to the results in Figures 8 and 9, it was possible to estimate that the double bonds were separated by the siloxane chain so that the effectiveness of the crosslinks formed in restricting the reactivity was less than that for the EGDM units, and this is a logical reason for the variations shown in Figure 8 and 9. Hill and coworkers^{30,35} also observed the same phenomenon

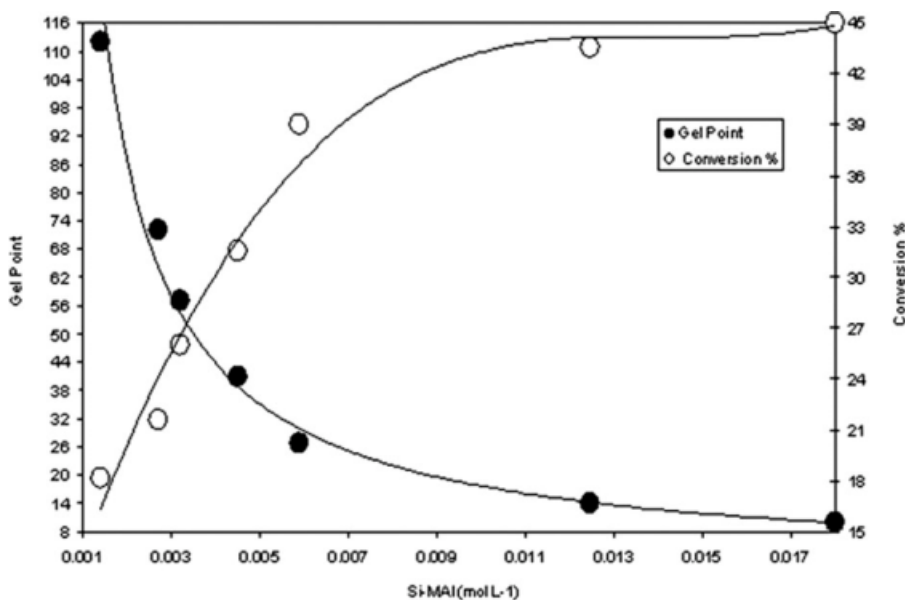


Figure 9 (○) Monomer conversion percentage and (●) gel point as functions of the Si-MAI concentration for MMA and EGDM copolymerization in EMK/DCM at 80°C (initial monomer concentration = 6 mol/L).

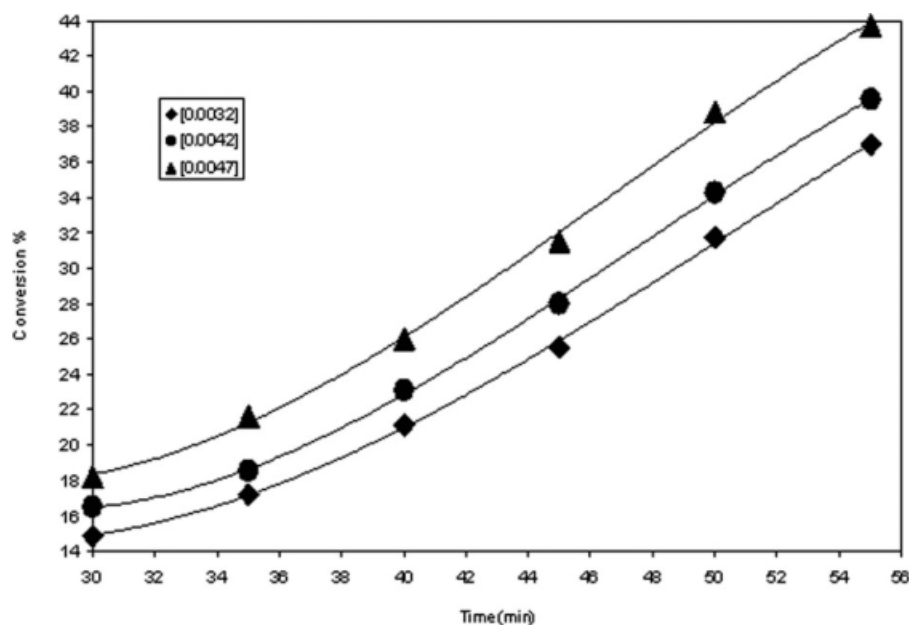


Figure 10 Effect of the initial Si-MAI concentration on the monomer conversion versus time at 80°C (initial monomer concentration = 6 mol/L): (◆) 0.0032, (●) 0.0042, and (▲) 0.0047 mol/L.

in the polymerization of siloxane-modified divinyl benzene prepolymers.

Effect of the Si-MAI concentration on the reaction rate

Although the copolymerization of MMA and EGDM has been well established,^{36–39} their copolymerization in the presence of Si-MAI has not been reported. It is possible that during the crosslinking copolymerization process this MAI will take part in

the polymer network. Figure 10 shows the effect of the Si-MAI concentration on the monomer conversion versus time where the initial monomer concentration was 6 mol/L. The rate of reaction increased with increasing Si-MAI concentration. According to the primary and secondary cyclization described in the previous section, the first macroradicals that formed were highly intramolecularly crosslinked and should have thus exhibited compact structures. The increase in silicone content increased the compactness of the structures formed, and this resulted

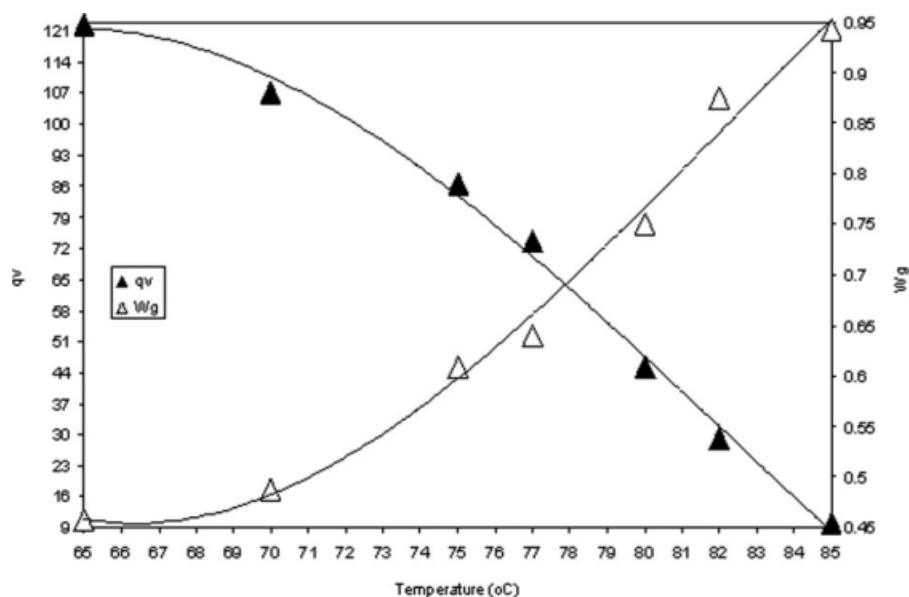


Figure 11 (△) W_g and (▲) q_v as functions of temperature for MMA and EGDM copolymerization in EMK/DCM (initial monomer concentration = 6 mol/L).

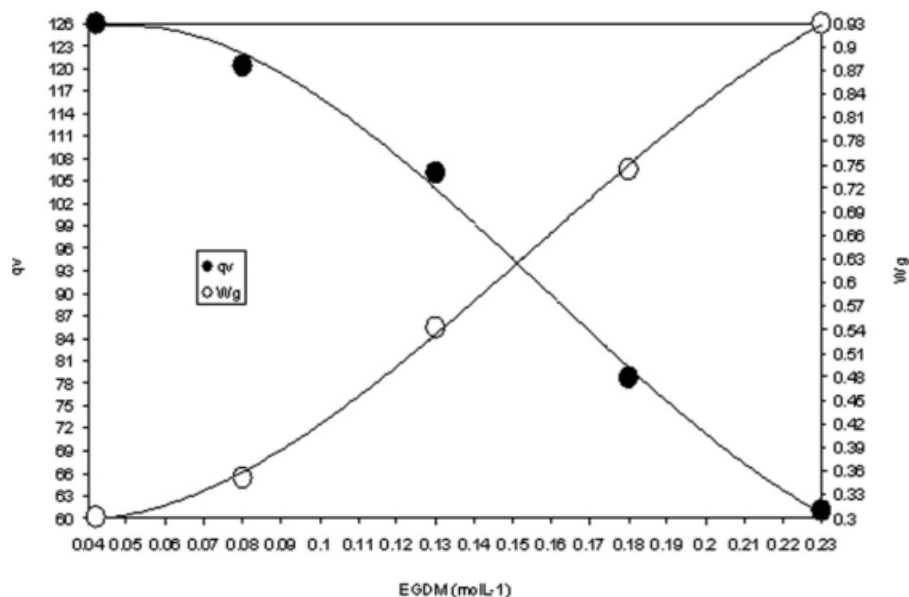


Figure 12 (○) W_g and (●) q_v as functions of the EGDM concentration for MMA, EGDM, and Si-MAI copolymerization in EMK/DCM at 80°C (initial monomer concentration = 6 mol/L).

in a decrease in the mobility of chain segments and, therefore, decreased the diffusion-controlled termination of radicals because of steric reasons. Furthermore, the rates of propagation and, consequently, copolymerization in a radical copolymerization reaction were related to the termination rate constant. As the amount of Si-MAI increased, it acted as a chain-transfer agent, and the rate of polymerization increased.

Effect of the temperature

W_g and q_v are shown in Figure 11 as a function of the reaction temperature for MMA and EGDM copolymerization. The temperature range studied at fixed concentrations of monomers and initiator was between 65 and 85°C with 6.63×10^{-3} mol/L Si-MAI.

According to Figure 11, W_g increased and q_v decreased with reaction temperature. This behavior was similar to that with MMA/EGDM, a crosslinking copolymerization system without silicone. Figure 11 also shows that there was very little swelling at 85°C and W_g was at its maximum value. Clearly, the reaction temperature was an important factor in these polymer systems.

Effect of the EGDM concentration

W_g and q_v are shown in Figure 12 as a function of the EGDM concentration for MMA and EGDM copolymerization. According to this figure, W_g increased and q_v decreased with EGDM concentration. Increasing the crosslinker content increased the compactness of the structures formed; this resulted in a decrease in the absorbability of the gels. These

phenomena were reflected in the decrease of q_v and increase in W_g .

Morphology of the polymer gels

The particle morphologies of the MMA/EGDM copolymers with and without Si-MAI were examined by SEM. The SEM micrographs of the copolymer particles of samples containing no silicone and 6.63×10^{-3} mol/L Si-MAI are shown in Figures 13 and 14, respectively. The surface of the MMA/EGDM copolymers without Si-MAI was considerably different from that of the copolymers with Si-MAI. Figure 13 exhibits a dense microstructure with many loose texture morphology. Figure 14 shows a homogeneous

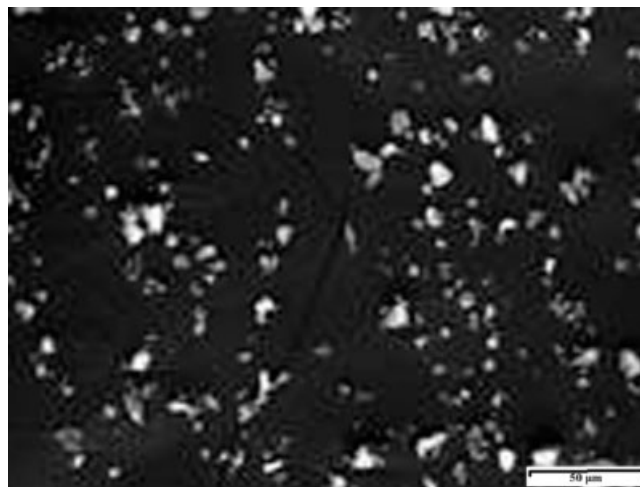


Figure 13 SEM picture of MMA/EGDM copolymers at 80°C (initial monomer concentration = 6 mol/L).

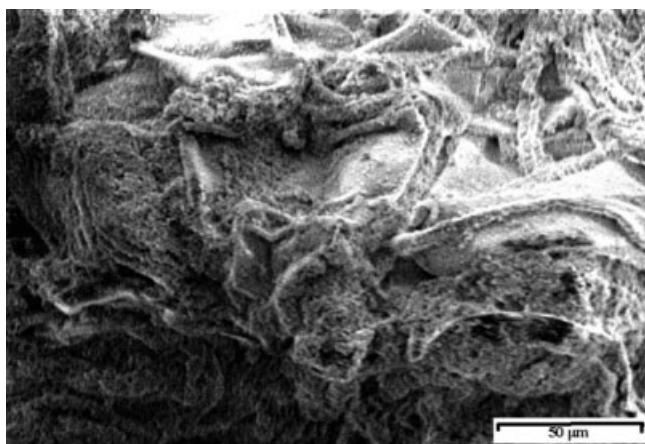


Figure 14 SEM picture of MMA/EGDM and Si-MAI copolymers at 80°C (initial monomer concentration = 6 mol/L).

morphology with the presence of a lot of cracks, probably due to solvent evaporation.

CONCLUSIONS

A silane-containing diamine, BADPS, was prepared by the condensation of PAP with DCDPS in the presence of TEA. Then, BADPS was condensed with ACPC to prepare MAIs containing silane units (Si-MAI). Also, a series of PMMA gels containing silane were derived by the solution free-radical crosslinking copolymerization of MMA and EGDM monomers initiated by these MAIs. They were then studied in a EMK/DCM solvent mixture (3 : 1 molar ratio) as the reaction medium at a total monomer concentration of 6 mol/L and 80°C. The following results were obtained:

1. Increasing the Si-MAI concentration resulted in a decrease in the gel point, W_g , and q_v and an increase in the conversion percentage.
2. Increasing the EGDM concentration resulted in a decrease in q_v and an increase in W_g .
3. Increasing the reaction temperature resulted in a decrease in the swelling degree and an increase in W_g .
4. The presence of Si-MAI moieties in the MMA/EGDM copolymers caused a homogeneous morphology with the existence of a lot of cracks, probably due to solvent evaporation.
5. FTIR analysis showed that silicone segments were present in the copolymer structures.

References

1. Hazer, B.; Erdem, B.; Lenz, R. W. *J Polym Sci Part A: Polym Chem* 1994, 32, 1746.

2. Ueda, A.; Nagai, S. *J Polym Sci Part A: Polym Chem* 1984, 22, 1621.
3. Hazer, B. *Macromol Chem* 1992, 193, 1086.
4. Ueda, A.; Nagai, S. *J Polym Sci Part A: Polym Chem* 1986, 24, 418.
5. Ueda, A.; Nagai, S. *J Polym Sci Part A: Polym Chem* 1987, 25, 3498.
6. Kinoshita, H.; Tanaka, N.; Araki, T.; Syoji, A.; Ooka, M. *Macromol Chem* 1993, 194, 839.
7. Kinoshita, H.; Tanaka, N.; Araki, T.; Ooka, M. *Macromol Chem Phys* 1994, 195, 425.
8. Tunca, U.; Yagci, Y. *J Polym Sci Part A: Polym Chem* 1990, 28, 1733.
9. Alli, A.; Hazer, B.; Menciloglu, Y.; Suzer, S. *Eur Polym J* 2006, 42, 750.
10. Alli, A.; Hazer, B.; Baysal, M. B. *Eur Polym J* 2006, 42, 3031.
11. Deniz, S.; Baran, N.; Akgun, M.; Akgun, N. A.; Dincer, S. *Turk J Chem* 2004, 28, 657.
12. Yildiz, U.; Capek, I. *Polymer* 2003, 44, 2200.
13. Nakamura, K.; Fujimoto, K.; Kawaguchi, H. *Colloid Surf A* 1999, 153, 201.
14. Yildiz, U.; Hazer, B. *Polymer* 2000, 41, 544.
15. Laverty, J. J.; Gardlund, Z. G. *J Polym Sci Part A: Polym Chem* 1977, 15, 2011.
16. Hizal, G.; Yagci, Y. *Polymer* 1989, 30, 725.
17. Hazer, B. *Macromol Chem Phys* 1995, 196, 1952.
18. Mishra, M. K. *Macromolecular Design Concept and Practice; Polymer Frontiers International: New York, 1994; p 307.*
19. Kim, D. K.; Lee, S. B.; Doh, K. S.; Nam, Y. W. *J Appl Polym Sci* 1999, 74, 926.
20. Nagamune, T.; Ueda, A.; Nagai, S. *J Appl Polym Sci* 1996, 62, 365.
21. Inoue, H.; Ueda, A.; Nagai, S. *J Polym Sci Part A: Polym Chem* 1988, 26, 1092.
22. Inoue, H.; Matsumoto, A.; Matsukawa, K.; Ueda, A.; Nagai, S. *J Appl Polym Sci* 1990, 40, 1938.
23. Hamurcu, E. E.; Hazer, B.; Misirli, Z.; Baysal, B. M. *J Appl Polym Sci* 1996, 62, 1426.
24. Hamurcu, E. E.; Hazer, B.; Baysal, B. M. *Polymer* 1997, 38, 2987.
25. Chang, T. C.; Chen, H. B.; Chen, Y. C.; Ho, S. Y. *J Polym Sci Part A: Polym Chem* 1996, 34, 2620.
26. Chang, T. C.; Chen, H. B.; Chiu, Y. S.; Ho, S. Y. *Polym Degrad Stab* 1997, 14, 57.
27. Chang, T. C.; Chen, H. B.; Ho, S. Y.; Chiu, Y. S. *J Macromol Sci Pure Appl Chem* 1996, 33, 1270.
28. Chang, T. C.; Chen, H. B.; Ho, S. Y.; Chiu, Y. S. *Polymer* 1996, 37, 2968.
29. Cheikhaldar, T.; Massardier, V.; Tighzert, L.; Pascault, J. P. *J Appl Polym Sci* 1998, 70, 627.
30. Hill, D. J. T.; Senake, P. P. M. C.; Pomery, P. J.; Toh, H. K. *Eur Polym J* 2000, 36, 253.
31. Okay, O.; Naghash, J. H.; Capek, I. *Polymer* 1995, 36, 2419.
32. Dusek, K. In *Developments in Polymerization*; Haward, R. N., Ed.; Applied Science: London, 1982; Vol.3, p 143.
33. Mao, R.; Liu, Y.; Huglin, M. B.; Holmes, P. A. *Macromolecules* 1995, 28, 6744.
34. Landin, D. T.; Macosko, C. W. *Macromolecules* 1988, 21, 851.
35. Hill, D. J. T.; Perera, M. C. S.; Popery, P. J.; Toh, H. K. *Polymer* 2000, 41, 9137.
36. Okay, O.; Funke, W. *Makromol Chem Rapid Commun* 1990, 11, 587.
37. Okay, O. *Makromol Chem* 1988, 189, 2217.
38. Okay, O.; Funke, W. *Makromol Chem* 1990, 191, 1573.
39. Naghash, J. H.; Momeni, A. R.; Alian, H.; Massah, A. R.; Ataie, S. *Polym Int* 2005, 54, 1571.