

Formation and Structure of Poly(methyl methacrylate) Gels Containing Triphenyl Vinyl Silane

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ABSTRACT: A series of Poly(methyl methacrylate) gels (PMMA) were prepared for making optical lenses by solution free radical crosslinking copolymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA), methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDM), and triphenyl vinyl silane (TPVS) comonomer systems. They were then studied in toluene at a total monomer concentration of 5 molL⁻¹ and 70°C. The conversion of monomer, volume swelling ratio, weight fraction, and gel point were measured as a function of the TPVS concentration, temperature, and chain transfer agents up to the onset of macrogelation. Structural characteristics of the gels were

examined by using equilibrium swelling in toluene, gel fraction, and Fourier-transform infrared (FTIR) analysis. The morphology of the copolymers was also investigated by Scanning electron microscopy (SEM). The dilution of the monomer mixture resulted in an increase in the gel point and swelling degree and a decrease in the percentage of conversion and gel fraction. Finally, TPVS is a compatible vinyl type silicone comonomer for this system. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2465–2472, 2010

Key words: gels; silicones; swelling; radical polymerization

INTRODUCTION

There are many chemical and biomedical applications such as optical lenses, which require polymer gels with excellent absorption and mechanical properties.^{1–21} These materials are prepared mainly by free radical copolymerization of monovinyl (MVM) and divinyl monomers (DVM) in a suitable solvent.^{22–30} The radical copolymerization of various silicone functional monomers and synthesis of new functional polymers with given structures and important properties have attracted considerable interest based on the improvement of properties and economical advantages. Optical lenses are one of the most important biomedical materials. These materials must be of high clarity and refractive index, with resistance to impact, abrasion, UV light, stiffness, gas-permeability, and surface wetting characteristics.^{31–33} 3-(1,1,2,2-tetrafluoroethoxy)-2-hydroxypropyl methacrylate, 2,2,2-trifluoroethyl methacrylate (TFEMA), 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate and diethylene glycol bis allyl carbonate are currently used for about 80% of the world plastic lenses.^{34,35} However, there is a need to experiment new monomers to control better the manufacturing process, and to be competitive in the market. For this purpose triphenyl vinyl silane has been used to be reacted with vinyl monomers on the

polymer chains. The purpose of adding triphenyl vinyl silane is to increase the refractive index of the polymer film or hydrogel without greatly affecting the glass transition temperature, elastic modulus, and tangent delta of them.

The major aim of this study was to use triphenyl vinyl silane (TPVS) and investigation the effects of this comonomer on free radical crosslinking copolymerization of TFEMA, methyl methacrylate (MMA), and ethylene glycol dimethacrylate (EGDM) networks by determining optimum polymerization conditions and evaluating the physical properties of the gels. In this article, an effort was made to elucidate evaluation of the weight fraction of gel and its equilibrium degree of swelling, conversion of monomer and gel point in terms of the functions of the chain transfer agents and TPVS concentrations. Accordingly, a series of experiments with varying amounts of TFEMA, MMA, EGDM, and silicone were carried out. The total monomer concentration was 5 molL⁻¹. Conversion of monomers and gel points were determined gravimetrically. This work was targeted towards using new monomers with better properties, cheaper price, and monitoring *in situ* conversion of these monomers. The author intend to use this copolymer for making optical lenses in the future projects.

EXPERIMENTAL

Materials and equipment

The monomer, MMA (Merck, Hohenbrunn, Germany), was washed with 10% aqueous potassium

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hydroxide to remove inhibitor, followed by several washings with deionized water. After drying successively with anhydrous sodium sulfate and 4 Å (40 nm) molecular sieves, it was distilled under reduced pressure. The middle fraction was then collected. The 2,2,2-trifluoroethyl methacrylate (TFEMA) (Harbin Xeogia Fluorine-Silicone Chemical Co.) were used as received. The cross linker, EGDM (Aldrich, Gillingham, UK), was washed similarly and then distilled under reduced pressure. The fraction boiling at about 77°C was collected. TPVS (Aldrich, Milwaukee wis USA), was analytical grade and used directly without further purification. The initiator, 2/2-azo bis (2-methyl-propionitrile) (AIBN, Merck, Hohenbrunn, Germany), was recrystallized three times from absolute methanol, followed by drying in a vacuum oven at room temperature. The polymerization solvent toluene (Merck, Hohenbrunn, Germany), was distilled twice over sodium. Fourier-transform infrared (FTIR) spectroscopy analysis was performed with a Nicolet Impact 400D Model spectrophotometer (Nicolet Impact, Madison, USA) using KBr pellets. The spectra were obtained over the wave number range 400–4000 cm⁻¹ at a resolution of 2 cm⁻¹ using an MCT detector with coaddition of 64 Scans. Scanning electron micrographs were taken on a JEOL-JXA 840 A SEM (JEOL, Boston, USA). 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. Refractive index measurements were performed with a Atago 1T Model refractometer (Atago 1T Model NAR-1T, input with DTM-1, Japan).

Polymerization procedure

Monomer solutions were prepared shortly before use by weighing the required amounts of MMA, TFEMA, EGDM, TPVS, AIBN, and toluene.

Each of the Pyrex ampoules with 10 mm internal diameter and about 70 mm length was filled with 3 g of monomer solution. After degassing by four successive freeze-thaw cycles using liquid nitrogen and a reduced pressure of 1.3 KPa the ampoules were torch sealed. The polymerization was initiated by immersing the ampoules in an oil bath maintained at a constant temperature, 70 ± 0.1°C and the reaction was quenched by thrusting the ampoules into liquid nitrogen. It was assumed that the surface-to-volume ratio of the ampoules was high enough to assure isothermal conditions. A typical recipe for the preparation of TPVS containing Poly (methyl methacrylate) (PMMA) gels and the process is given in Table I and Scheme 1, respectively.

The homologous series of Polymer gels prepared in this way allowed systematic variation of the toluene, MMA, and TPVS concentrations, while the

TABLE I
Polymerization Recipe

Run	MMA (molL ⁻¹)	EGDM (molL ⁻¹)	TFEMA (molL ⁻¹)	TPVS (molL ⁻¹)
1	3.75	0.25	1.00	0.00
2	3.72	0.25	1.00	0.03
3	3.70	0.25	1.00	0.05
4	3.67	0.25	1.00	0.08
5	3.65	0.25	1.00	0.10
6	3.62	0.25	1.00	0.13
7	3.60	0.25	1.00	0.15
8	3.57	0.25	1.00	0.18
9	3.55	0.25	1.00	0.20
10	3.50	0.25	1.00	0.25

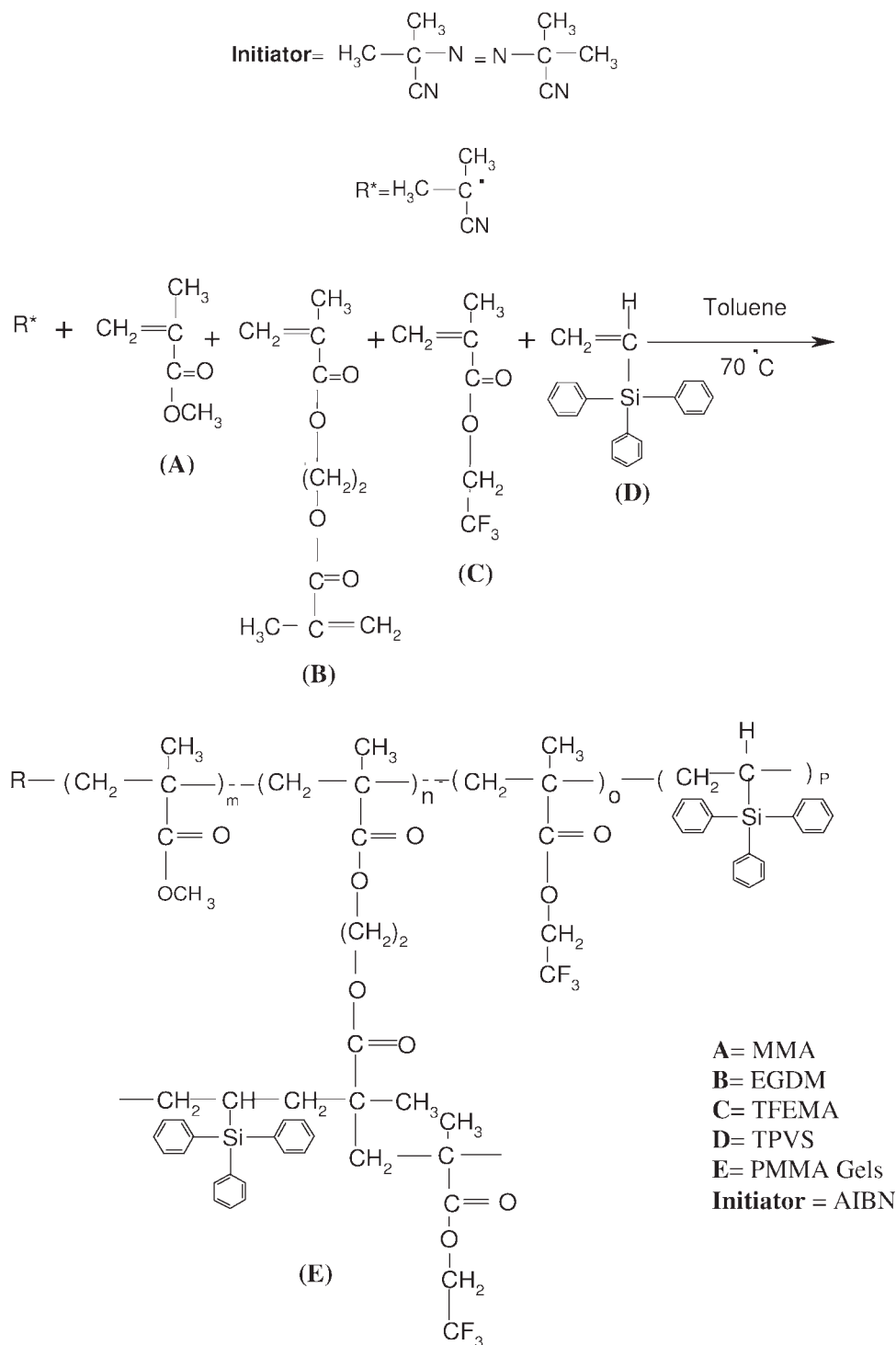
[M]₀ = 5 molL⁻¹, [AIBN] = 7 × 10⁻³ mol L⁻¹, T = 70°C, solvent = toluene.

amount of EGDM and TFEMA, were kept constant. The polymer samples for conversion measurements were obtained by a gravimetric technique. For this purpose, the monomers and toluene were pipetted into a 100 mL three-neck round-bottomed flask containing a Teflon covered magnetic stirring bar, and the appropriate amount of AIBN 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 70°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 into 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 drop wise into an agitated solution of methanol. The conversion of monomer was determined 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 that at which the mixture was not soluble in toluene. The number of polymer particles (*N_T*) was calculated from the monomer conversion (*X_M*), and the volume-average diameter of the polymer particles (*d_v*) was determined by SEM, using the following equations:

$$d_v^3 = \frac{\sum n_i d_i^3}{\sum n_i} \quad (1)$$

$$N_T = \frac{6M_0 X_M}{\pi d_v^3 \rho_p} \quad (2)$$

where *M₀* is the initial total monomer concentration, *n_i* is the number of particles, and *ρ_p* is the density of the polymer. The volume-average diameters of the polymers were found to be 3200, 4250, and 9700 nm for MMA, MMA, TFEMA, EGDM, and MMA, TFEMA, EGDM, TPVS polymer and copolymers,



Scheme 1

respectively. The reproducibility of the kinetics data was checked by repeating the experiments and all data considered in this article are an average of at least three measurements.

Extraction of the sol fraction

Toluene was chosen as the extraction solvent and employed at room temperature. The crude gels, 10

mm in diameter, were cut into samples of 10–25 mm length. Each sample was placed in an excess of toluene 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 de-swollen in a series of toluene/methanol mixtures with increasing methanol content. They were then washed several times with

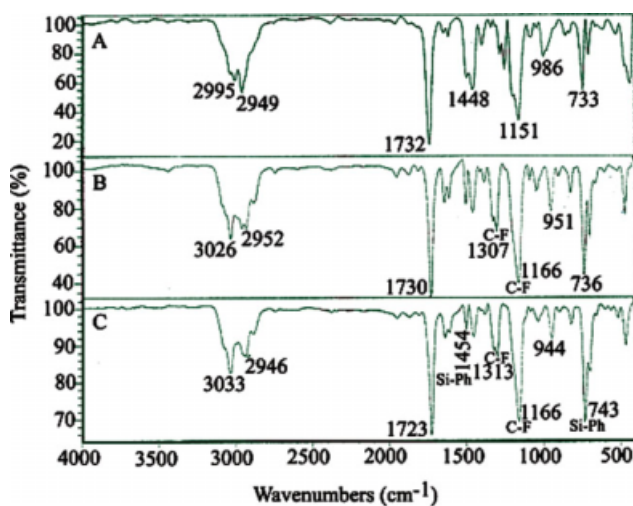


Figure 1 FTIR spectrum of A: poly(MMA), B: poly(MMA, TFEMA, and EGDM), and C: poly(MMA, TFEMA, EGDM, and TPVS). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

methanol and dried at room temperature under vacuum to constant weight. The amount of soluble polymer in toluene solution was determined gravimetrically after evaporation and precipitation in methanol. The weight fraction of gel (W_g) was calculated as

$$W_g = \frac{g}{g + s} \quad (3)$$

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

Swelling measurements

The swelling measurements were carried out in toluene at room temperature. To determine the equilibrium degree of swelling, the networks were immersed in toluene for at least 3 weeks, and the swelling equilibrium was tested 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 earlier, under vacuum to constant weight. The extent of swelling was characterized by the volume swelling ratio (q_v), which was calculated as:

$$q_v = 1 + \frac{(q_w - 1)\rho_p}{\rho_s} \quad (4)$$

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

RESULTS AND DISCUSSION

FTIR analysis

The structure of the copolymers before the gel point was determined by FTIR spectroscopy. Figure 1 shows the FTIR spectra of (A) MMA, (B) MMA, TFEMA, EGDM, and (C) MMA, TFEMA, EGDM, TPVS polymer and copolymers, respectively. Bands in the region of (2995–2949 cm^{-1}) and the nonhydrogen bonded carbonyl bands of acrylate groups (1732 cm^{-1}) in the spectra indicate $-\text{CH}_2$ -bridges and C–H stretching of PMMA network, respectively. The characteristic bands due to Si-ph (1454–743 cm^{-1}) of silane units, assigned to TPVS containing PMMA gels. In the spectra of C, the characteristic absorption of C=C bond at 1640 cm^{-1} disappeared, indicating that MMA, TFEMA, EGDM, and TPVS monomers had been copolymerized. The absorption peak of C–F bond at 658 cm^{-1} (CF_3 rocking), 1166 cm^{-1} and 1313 cm^{-1} demonstrated further that TFEMA had been incorporated into the polymer chains.

The same analysis was repeated a total of three times for each sample and it was concluded that by these spectra, it is clear that TPVS has been successfully copolymerized to poly MMA/EGDM/TFEMA.

Effects of TPVS concentration on the MMA/EGDM/TFEMA gel properties

Increasing the TPVS concentration resulted in a decrease in the weight fraction of gel and an increase in the swelling degree (Fig. 2). Also, the conversion percent showed a drastic decrease while the gel point showed an increase (Fig. 3). TPVS with one double bond can react with MMA, TFEMA, and EGDM. It is well known that the free radical crosslinking copolymerization system involves three types of vinyl groups: those on vinyl and divinyl monomers (DVM) and those on polymer chains, ie Pendant vinyls.^{36–44} Accordingly, the polymerization system can be considered as a special case of

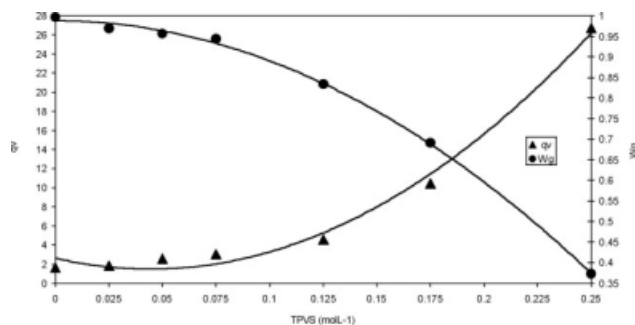


Figure 2 Weight fraction (\bullet) W_g and the equilibrium volume swelling ratio of the gel in toluene (\blacktriangle) q_v plotted as functions of the TPVS concentration for MMA, TFEMA, EGDM, and TPVS copolymerization in toluene at 70°C with $7 \times 10^{-3} \text{ mol L}^{-1}$, AIBN, $[M]_0 = 5 \text{ mol L}^{-1}$.

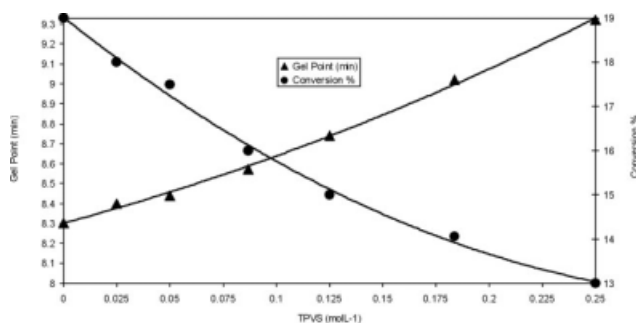


Figure 3 Monomer conversion and the gel point shown as function of the TPVS concentration for MMA, TFEMA, EGDM, and TPVS copolymerization in toluene at 70°C with $7 \times 10^{-3} \text{ molL}^{-1}$ AIBN, $[M]_0 = 5 \text{ molL}^{-1}$. Experimental data are shown as (●) conversion % and (▲) gel point.

copolymerization, in which one of the vinyl groups (pendant vinyls) is created during the course of the reaction when the vinyl on the 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 macroradical attacks the pendant vinyl group in the same kinetic chain, while with multiple crosslinking it is formed if the radical attacks the pendant double bonds on other chains already chemically connected to the growing radical^{1,45} (Fig. 4). It should be noted that cyclization and multiple crosslinking have been redefined as primary and secondary cyclization, respectively.⁴⁶ 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 reactivities even to the extent that they may be considered to be trapped and unavailable for reactions. In the present system, the EGDM cross linker contains two double bonds and, according to the result in Figure 2, it is possible to estimate that double bonds may appear as pendant to the polymer chain so that the effectiveness of the cross links formed in restricting the reactivity was less than that for the EGDM units. It is worth mentioning that the presence of TPVS causes a decrease in the crosslinking degree, consequently the compactness of the gels decrease. In this case swelling degree will be increased and this is a logical reason for variations in Figures 2 and 3. Hill et al.^{6,44} also observed the same phenomenon in the polymerization of siloxane-modified divinyl benzene prepolymers.

Effects of TPVS concentration on the reaction rate

Although copolymerization of MMA and EGDM has been well established^{37,41,42} their copolymerization in

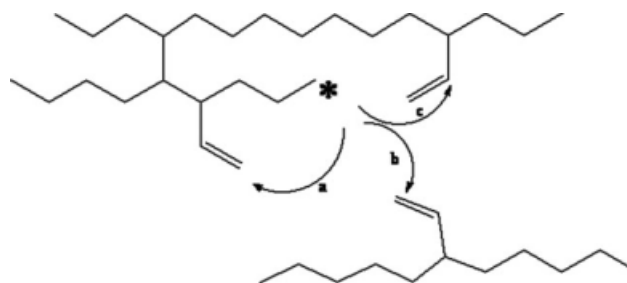


Figure 4 Schematic representation of the processes of cyclization (a), crosslinking (b), and multiple crosslinking (c) in free-radical crosslinking copolymerization.

the presence of TPVS has not been reported. However, this work has demonstrated that this monomer will make part of the polymer network during crosslinking copolymerization process via double bonds. Figure 5, shows the effect of TPVS concentration on the monomer conversion versus time where the initial monomer concentration was 5 molL^{-1} . It can be observed that the rate of reaction decreased with increasing amounts of TPVS. According to the primary and secondary cyclization described in the previous section, the first macroradicals formed were highly intramolecularly crosslinked, and should thus exhibit compact structures. The increase in silicone content increases the compactness of the structures formed and this resulted in a decrease in the mobility of chain segments and therefore decreased the diffusion-controlled termination of radicals owing to steric reasons. Furthermore, the rates of propagation and consequently copolymerization in a radical copolymerization reaction are inversely related to the termination rate constant. As the amount of TPVS increased, the rate of polymerization decreased.

Effect of temperature

The weight fraction of gel (W_g) and its equilibrium volume swelling ratio in toluene, (q_v), are shown in

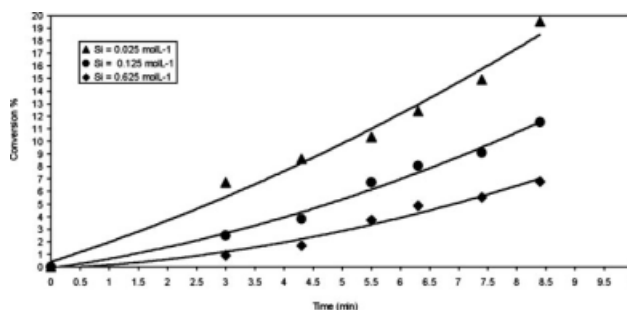


Figure 5 The effect of initial TPVS concentration on monomer conversion versus time histories at (▲) 0.025; (●) 0.125 and (◆) 0.625 molL^{-1} , $[M]_0 = 5 \text{ molL}^{-1}$, $[I]_0 = 7 \times 10^{-3} \text{ molL}^{-1}$.

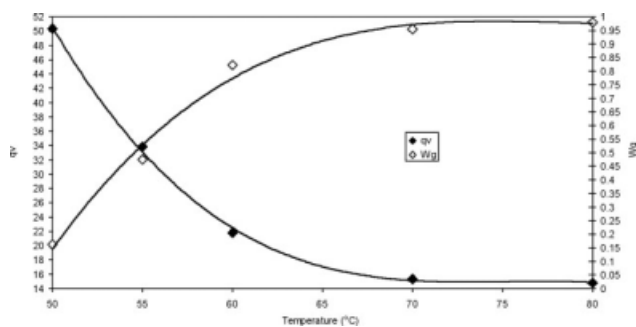


Figure 6 Weight fraction (\diamond) W_g and the equilibrium volume swelling ratio of the gel in toluene (\blacklozenge) q_v plotted as functions of the temperature for MMA, TFEMA, EGDM, and TPVS copolymerization in toluene at 70°C with $7 \times 10^{-3} \text{ mol L}^{-1}$ AIBN, $[M]_0 = 5 \text{ mol L}^{-1}$.

Figure 6 as a function of the reaction temperature for MMA, TFEMA, EGDM, and TPVS copolymerization. The temperature range studied at fixed concentration of monomers and initiator was between 50 and 80°C with 0.025 mol L^{-1} TPVS. According to this Figure, W_g increased and q_v decreased with reaction temperature. Any increase in temperature leads to an increase in the motion of the particles and this in turn leads to an increase in the crosslink density. This creates more compact gels and as a result, q_v decreases. Figure 6 also shows that there is no any swelling at 80°C and W_g is on its maximum value. Clearly, the reaction temperature is an important factor in these polymer systems.

Effect of chain transfer agent

The silicone contained polymer gels of MMA/TFEMA/EGDM in toluene using AIBN at 70°C in presence of different concentrations of CCl_4 and *t*-BuOH as chain transfer agents were performed. By increasing the concentration of both chain transfer agents the swelling ratio increased and gel fraction decreased.

The data are graphically represented in Figures 7 and 8 for *t*-BuOH and CCl_4 , respectively. In some

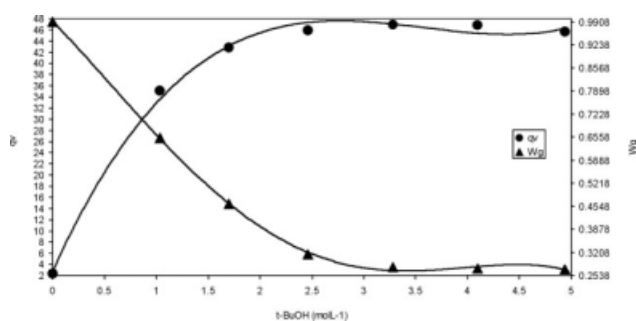


Figure 7 Weight fraction (\blacktriangle) W_g and the equilibrium volume swelling ratio of the gel in toluene (\bullet) q_v plotted as functions of the (*t*-BuOH) concentration for MMA, EGDM, TFEMA, and TPVS copolymerization in toluene at 70°C with $7 \times 10^{-3} \text{ mol L}^{-1}$ AIBN, $[M]_0 = 5 \text{ mol L}^{-1}$.

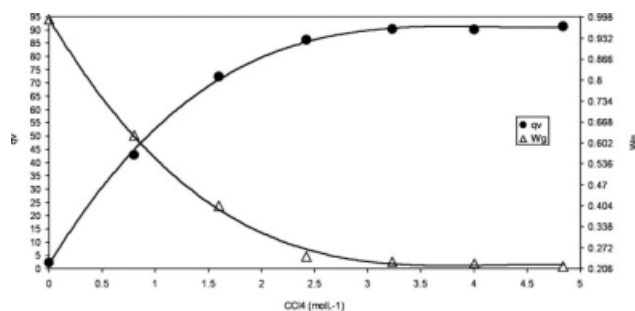


Figure 8 Weight fraction (Δ) W_g and the equilibrium volume swelling ratio of the gel in toluene (\blacktriangle) q_v plotted as functions of the (CCl_4) concentration for MMA, EGDM, TFEMA, and TPVS copolymerization in toluene at 70°C with $7 \times 10^{-3} \text{ mol L}^{-1}$ AIBN, $[M]_0 = 5 \text{ mol L}^{-1}$.

cases termination may be brought about by transfer reactions. In this type of reactions, though the growth of one polymer chain is stopped due to formation of dead polymer as in coupling or disproportionation reaction, yet there is a simultaneous generation of a new free radical that is capable of initiating a fresh polymer chain growth. These reactions commonly take place in free radical polymerization. Typical chain transfer agents including CBr_4 and CCl_4 , in the interactions in which it is halogen atoms that are transferred, and thiols which have the form of RSH , where R is an alkyl chain, and involve hydrogen abstraction to form RS , through which reinitiation occurs. Basically, it is stated that transfer does not affect the overall rate of polymerization. However, in this case transfer reactions are of major kinetic importance, as well as often dominant in controlling the molecular weight in free radical polymerization. In addition, the distribution of small free radicals, and hence the transfer reaction can play important parts in shaping the overall rate of polymerization. Additionally, chain transfer in heterogeneous polymerizations could promote inter-phase migration of free radical species: i.e., the increase of the rate of exit and consequently a decrease in polymerization rate. In the previous section it has been demonstrated that TPVS act as a chain transfer agent and the rate of polymerization reaction decreases. This phenomenon leads to an

TABLE II
Morphologies of Polymer and Copolymer Particles with and Without Silicone

Polymer and copolymer	d_v (nm)	X_M	$N_T \times 10^{10}$	ρ (g/cm^3)
(A) MMA	3200	0.74	4.30	0.60
(B) MMA + EGDM + TFEMA	4250	5.84	50.80	0.15
(C) MMA + EGDM + TPVS + TFEMA	9700	0.97	0.30	0.40

$$[M]_0 = 5 \text{ mol L}^{-1}, T = 70^\circ\text{C}, [\text{AIBN}] = 7 \times 10^{-3} \text{ mol L}^{-1}.$$

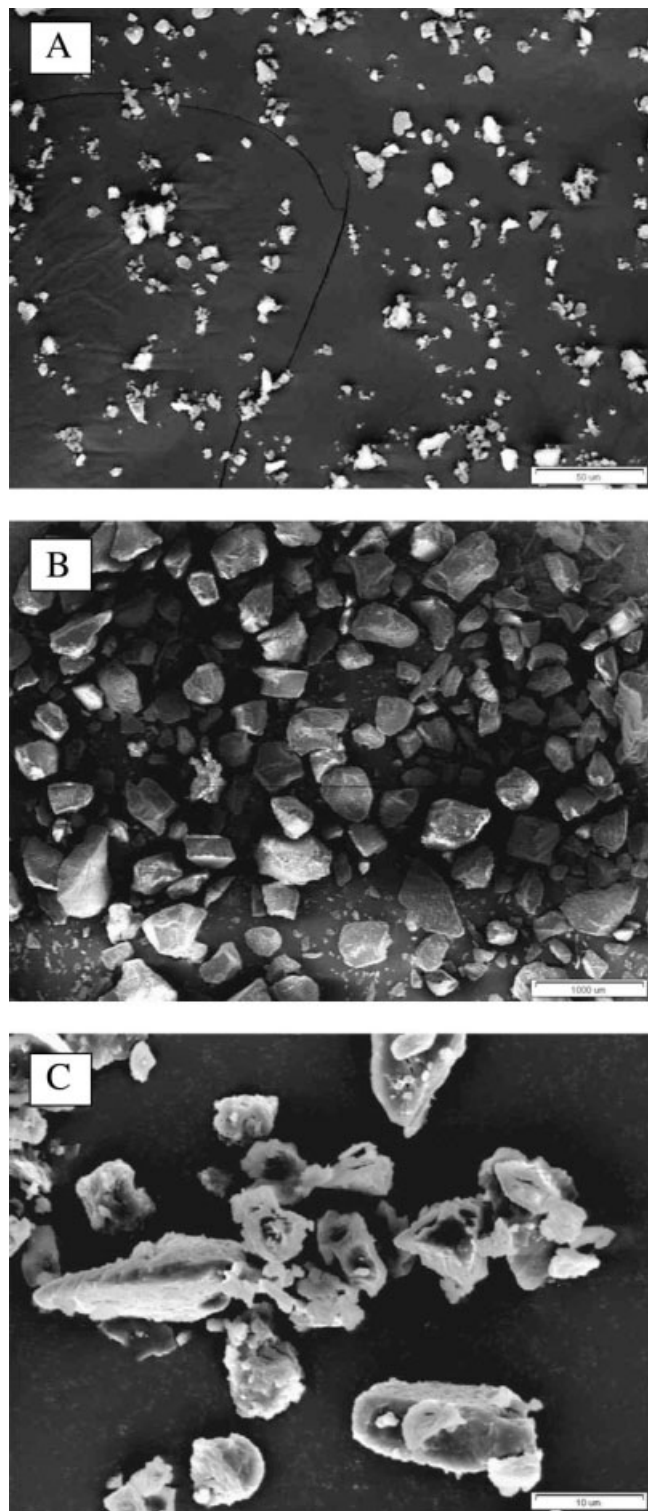


Figure 9 SEM pictures of (A) MMA, TFEMA, EGDM copolymer, (B) with 3.6, and (C) with 18.6 wt % TPVS, $[M]_0 = 5 \text{ molL}^{-1}$, $[I]_0 = 7 \times 10^{-3} \text{ molL}^{-1}$.

increase in swelling ratio and a decrease in gel fraction. The findings of this study reveal that the fluctuations shown in Figures 7 and 8 seem to be correct and logical.

Morphology of polymer particles

The particle morphologies of MMA/EGDM/TFEMA copolymers with and without TPVS were examined by SEM, and the data are shown in Table II. The SEM micrographs of the copolymer particles of samples containing no TPVS, 0.13 and 0.25 molL⁻¹ TPVS are shown in Figure 9(A–C) and the volume-average particle diameters were found to be 3200, 4250, and 9700 nm, respectively. It is clear that the MMA/EGDM/TFEMA copolymers had very small particles compared with TPVS-contained samples, and by increasing the TPVS concentration the particle size increases and their size distributions get narrower. TPVS with one double bond can polymerized with acrylic monomers. In TPVS, the phenyl groups are sterically hindered and increased the bulkiness around the center of the reactions. On the other hand, phenyl is an electron-withdrawing group and therefore destabilized the reaction. The overall effect of phenyl groups is to decrease the rate of reactions. Also by increasing the TPVS concentration, conversion percent decreases. The presence of TPVS moiety in the copolymerization causes inhibition of the reaction and consequently the irregular particle sizes will be obtained. The monomers used in this study have vinyl groups and probably a part of these vinyl groups can not contribute the copolymerization reaction and stayed as pendant vinyl groups. This phenomenon also might affect on the morphology. Although I did not discuss the reactivity ratio of different monomers in this work, but it can also affect on the particle sizes and morphologies.

Effect of TPVS concentration on the refractive index measures of MMA polymer and copolymers

Table III, shows the effect of TPVS concentration on the refractive index measures of MMA polymer and copolymers, respectively. According to this Table, the presence of TPVS causes an increase in the refractive index measures and by increasing TPVS concentration these measures increase.

TABLE III
Refractive Index Measurements (n_D^{25})

Polymer and copolymer	Refractive index n_D^{25}
(A) MMA	1.48
(B) MMA + EGDM	1.49–1.50
(C) MMA + EGDM + TFEMA	1.50
(D) MMA + EGDM + TFEMA + TPVS	1.51–1.53

$[M]_0 = 5 \text{ molL}^{-1}$, $[AIBN] = 7 \times 10^{-3} \text{ molL}^{-1}$, $T = 70^\circ\text{C}$, solvent = toluene.

CONCLUSIONS

Free radical crosslinking copolymerization of silicone containing MMA/TFEMA/EGDM was evaluated. The copolymerizations were carried out in toluene at a total monomer concentration of 5 molL⁻¹ and 70°C. The following results were obtained:

1. Increasing TPVS concentration resulted in a decrease in polymerization rate and an increase in swelling degree and gel point.
2. Lowering the monomer concentration resulted in a decrease in the conversion % and gel fraction, and an increase in the gel point and swelling degree.
3. The presence of TPVS comonomer in the MMA/TFEMA/EGDM copolymers resulted in the formation of larger particles compared without TPVS and also an increase in the refractive index measures.
4. These copolymers have potential to be used as optical lenses and further work on these copolymers will be reported later.
5. The presence of TPVS in these copolymers causes an increase in the refractive index measures.

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