

Crosslinker Reactivity and the Structure of Superabsorbent Gels

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ABSTRACT: A ¹³C-labeled crosslinker (trimethylolpropane triacrylate, TMPTA) was synthesized and copolymerized with acrylic acid while monitoring the relative rates of reaction of the crosslinker and acrylic acid by ¹³C-NMR. This allowed easy quantification of the concentration of the minor component (crosslinker) in the polymer and monomer mixture to levels as low as 0.02%. Polymerizations were conducted in 5 mm NMR tubes under varied temperature, percent neutralization (pH), and percent solids. Reactivity ratios were determined from the rates of incorporation of the components into the gel by use of the integrated form of the copolymerization equation, and their sensitivity to the above variables was quantified. The relative rate of incorporation of the crosslinker into the gel was exceedingly fast. The reactivity ratio, r_1 for acrylic acid, varied from 0.31 (65% neutralization) to 0.77 (unneutralized). The reactivity ratio was affected by the percent solids (solvent effect), but was insensitive to temperature over the range of 55–80°C. It was observed that all of the double bonds of TMPTA were incorporated into gel network as opposed to prior models predicting only two bonds reacting. The reported inefficiency of TMPTA is postulated to be caused by a solubility problem in the monomer mixture. Very low levels of extractables were found in the products even though the crosslinker was consumed by 70% conversion. Based on these data, we propose that a major component of the gel network is graft polymer that forms late in the polymerization onto the crosslinked gel formed earlier. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 439–451, 1997

Key words: polyacrylic acid; superabsorbent; ¹³C-NMR; crosslinker; reactivity ratio

INTRODUCTION

A wide variety of vinyl crosslinkers have been used to form crosslinked networks with acrylic acid. In bulk polymerizations or organic solvent systems the choice of crosslinkers is quite broad. Almost any multivinyl monomer will work, including crosslinkers such as divinyl benzene and

diallyl phthalate. However, in water-phase polymerizations, solubility of many crosslinkers becomes marginal and when the acid is partially neutralized, the problem is ever greater. Common vinyl crosslinkers for superabsorbents include *N,N*-methylene and ethylene bis(meth)acrylamide, triallyl amine, ethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, allyl(meth)acrylate, and various polyethylene oxide extended polyvinyl (meth)acrylates. Some of the more commonly used crosslinkers are shown in Figure 1.

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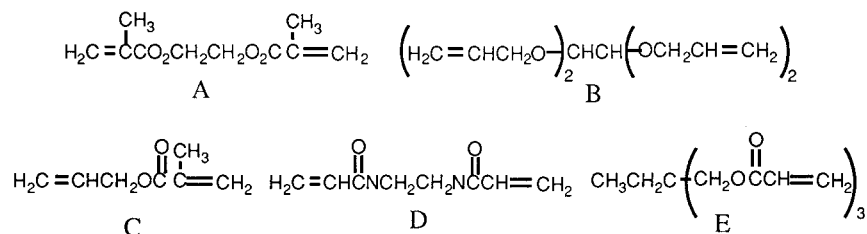


Figure 1 Structure of common crosslinkers used in superabsorbent products. (A) Ethylene glycol dimethacrylate; (B) tetraallyloxyethane; (C) allylmethacrylate; (D) *N,N*-ethylene bisacrylamide; and (E) trimethylolpropane triacrylate.

These crosslinkers are used at levels ranging from 0.01 to 2.0%, usually about 0.05–1.0% to provide superabsorbents with high swelling capacity and reasonably low soluble polymer content.

The swelling characteristics of superabsorbent materials are controlled by a balance of opposing forces, swelling forces driven by osmotic pressure, and restoring forces from a variety of physical, covalent, or ionic crosslinks. The osmotic forces result from the partially ionized acrylic acid units of the polymer chain. The crosslinks are typically incorporated during the polymerization by the use of copolymerized multivinyl crosslinkers such as those in Figure 1. The ultimate structure of the crosslinked polyacrylic acid network is influenced by both polymerization factors, such as the amount and type of multifunctional crosslinker, as well as post treatment reactions.

Network formation during the solution polymerization of partially neutralized acrylic acid containing a multifunctional acrylate or methacrylate crosslinker can be viewed as a copolymerization reaction. The Flory–Stockmayer theory has been used to predict the gel network buildup of a crosslinking polymerization system.^{1,2} Many side reactions, such as intrachain cyclization, decrease the efficiency of the crosslinker and result in a gel point later in the polymerization than would be predicted by theory and in networks less crosslinked than would be predicted from the number of potential crosslink sites. This deviation from theory can be significant at high crosslinker levels, such as used in styrene divinylbenzene copolymers where intramolecular cyclization is believed to occur. At very high levels of crosslinker and at high conversion, pendant vinyl groups were found to be less reactive and not utilized in forming the network. Local steric effects and lack of chain mobility were proposed for their lack of reactivity.³ Okay et al.⁴ determined that almost half of the pendant double bonds in a mixture of ethylene glycol dimethacrylate (EGDM) in

methyl methacrylate (MMA) were consumed by internal cyclization reactions when the mole fraction of EGDM was 0.126 to 0.256. However, Landin and Macosko showed that for low levels of EGDM in methyl methacrylate, the rate of intramolecular cyclization was very low.⁵ Tobita and Hamielec observed very high levels of cyclization (ca. 80%) in acrylamide/bisacrylamide copolymerization when the total monomer content of the solution was low (6%).⁶ Intramolecular cyclization increases with polyvinyl monomer content, low monomer content, and high conversion. When a large excess of the monovinyl monomer is present, such as at lower conversion, the intramolecular cyclization rate is very low. Because of the high monomer content and the low crosslinker levels used in typical superabsorbent processes, there is a reduced probability of this inefficient side reaction, especially during the initial part of the polymerization process.

In order to understand the distribution of crosslinks in the network, one must know the reactivity ratios of all of the various double bonds in the system with each of the other types of double bonds. This would include sodium acrylate (and/or acrylic acid), the initial double bonds of the crosslinker, and the various double bonds that are pendant to the polymer chain after incorporation of the crosslinker (Fig. 2). Using trimethylolpropane triacrylate (TMPTA) as a model crosslinker, initially all three of the double bonds would be expected to have the same reactivity with acrylic acid, but once incorporated into the polymer network through one of the double bonds, it was proposed that the second and third double bonds will be less reactive. In fact, it is believed that the third double bond is not reactive at all in preneutralized acrylic acid polymerizations, because of steric hindrance or shielding, and thus remains as a dangling double bond.⁷ This earlier model of gel structure was based on the inefficient crosslinking seen with TMPTA, resulting in gels with

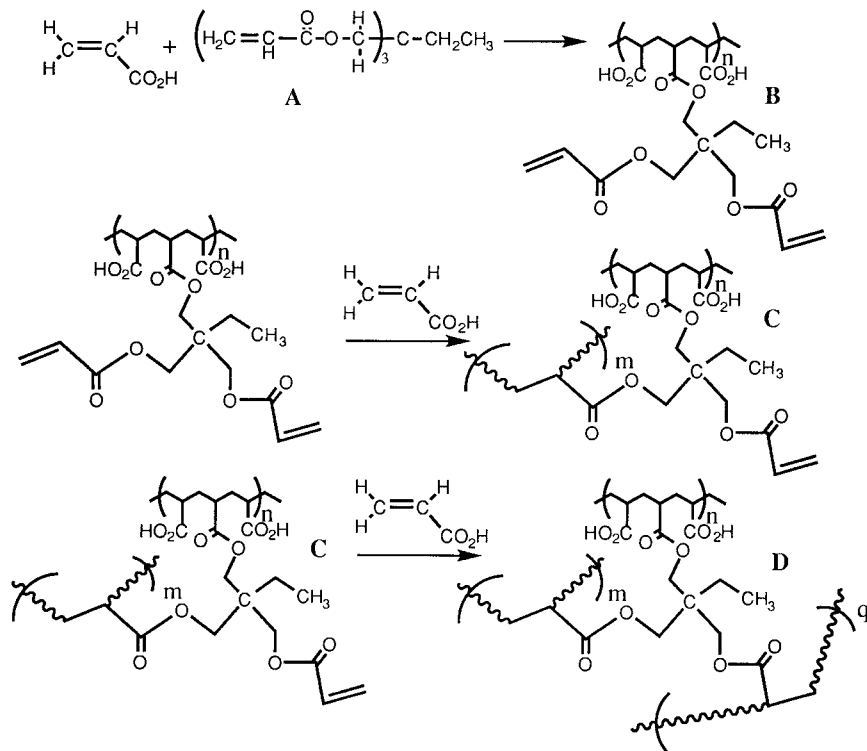


Figure 2 Reactions of TMPTA double bonds to form a crosslinked network.

swelling and moduli similar to that of gels prepared using divinyl crosslinkers at a comparable molar content. In the study reported here, the previous model has been shown to be in error, and explanations for the prior observations are presented.

In a copolymerization reaction, the reactivity ratios r_1 and r_2 (functional groups in this work) are defined by; $r_1 = k_{p11}/k_{p12}$ and $r_2 = k_{p22}/k_{p21}$, where k_{pij} is the rate constant for the reaction of a growing polymer chain containing a terminal M_i unit reacting with monomer functional group M_j . When r_1 is greater than 1, M_1 prefers to react with itself and not the other monomer group. If $r_1 = 1$, then the growing chain with an M_1 group on the end reacts equally with M_1 and M_2 . Very frequently r_1 is less than 1, indicating that when an M_1 group is on the end of the chain, it will tend to favor adding to the other monomer instead of one of its own kind. This type of behavior can lead to alternating copolymers under certain circumstances. The composition of a copolymer is, thus, controlled by both the reactivity ratios of the monomers and the initial monomer concentrations. The reactivity ratio of acrylic acid with several monomers is shown in Table I.

Several techniques have been developed to de-

termine the reactivity ratios of monomers.¹² The most frequently cited method is that of Kelen–Tudos,^{13,14} where monomer feed mixtures of varying composition are polymerized to low conversion and the resultant polymer composition is measured. The values of r_1 and r_2 are then determined graphically from the data. The Kelen–Tudos method is useful but requires multiple polymerization runs as well as characterization of the copolymer composition from each mixture. Quantification of the diad and triad fractions of copolymers by NMR is also a useful method to obtain the reactivity ratios.^{15–17} This present investigation of AA-TMPTA reactivity ratios used the integrated form of the copolymer equation.¹⁸ To determine r_1 and r_2 by this method, values that best describe copolymer composition–conversion profiles were selected.

Reactivity ratios are generally not influenced by the reaction medium,¹⁹ but for very polar monomers in polar solvents, changes in reactivity as the medium changes have been observed.^{20,21} Ionizable monomers such as acrylic acid exist in both the protonated form and ionized form, and the two species exhibit different reactivity and sensitivity to pH. The reactivity ratio observed for acrylic acid reflects the relative amount of the two

Table I Reactivity Ratios of Acrylic Acid in Radical Copolymerization

| M_1 | r_1 | M_2 | r_2 | T (°C) | Solvent |
|----------------------------|-------|---------------|-------|----------|---------|
| Acrylic acid ⁹ | 0.25 | Styrene | 0.15 | 60 | None |
| Acrylic acid ⁹ | 0.05 | Styrene | 1.6 | 60 | DMF |
| Acrylic acid ⁹ | 0.13 | Styrene | 0.30 | 60 | Benzene |
| Acrylic acid ¹⁰ | 3.25 | Acrylonitrile | 0.34 | 40 | Water |
| Acrylic acid ¹¹ | 0.29 | MMA | 1.13 | 65 | Benzene |

forms present in solution. Both monomer concentration and solvent influence the extent of ionization and, thus, the reactivity ratio of monomers such as acrylic acid.^{22,23} Ponratnam²⁴ reported a maximum for r_1 (0.92) at a pH of 2 and a minimum (0.33) at pH 7 in the copolymerization of acrylic acid (M_1) and acrylamide. He also observed a similar effect of pH in the copolymerization of acrylic acid and *N*-vinyl pyrrolidone.²⁵

Temperature is another factor that has been investigated for its effect on reactivity ratios. Typically, temperature has very little influence. When a temperature effect is obtained, the observation has been that an increase in temperature causes the reactivity ratios to approach unity.²⁶ This results from lower selectivity at higher temperatures. Because activation energies are low for radical propagation reactions, temperature would be expected to have only a minor influence on their relative rates and, thus, the reactivity ratios.

In this study a sensitive analytical technique was needed to quantify the relative concentrations of each material and type of double bond in order to determine the reactivity ratios of the various monomeric and crosslinker double bonds. The use of infrared spectroscopy,³ NMR,^{4,27} and titration techniques⁴ have been attempted previously to address this problem. NMR was insensitive, even at high concentrations of the crosslinker, and none are sufficiently sensitive to quantify the components at the low levels (<1%) normally used in crosslinked superabsorbent resins. For this reason, a ¹³C-labeled crosslinker (TMPTA) was prepared that enhanced the NMR detection limits by a factor of almost 100 and allowed the polymerization process to be studied at low concentrations of crosslinkers.

The goal of this study was to determine the reactivity ratios of acrylic acid with typical acrylate crosslinkers that could then be used to better understand and model the crosslinked network made in a typical superabsorbent polymerization process. Another goal was to develop a methodol-

ogy to determine reactivity ratios that would be useful for other crosslinked systems. In studying this copolymerization reaction, it was also hoped that the cause of the inefficient use of the double bonds of trivinyl crosslinkers (TMPTA) could be determined and provide direct evidence for the presence or absence of unreacted double bonds in the network, such as that in structures B and C of Figure 2.

EXPERIMENTAL

To enhance the detection of the acrylate ester crosslinker by ¹³C-NMR during the polymerization, the carbonyl carbon was labeled with ¹³C following the procedure outlined in Figure 3.

The solvents and reagents used were either of very high purity and free of water (trace amounts only) and, in some cases, were distilled and stored over molecular sieves; methylene chloride (CH₂Cl₂) (HPLC–GC/MS grade: distilled and stored over molecular sieves, Fisher), triethyl amine (ET₃N) (99+; then distilled and stored over molecular sieves), dimethyl formamide (DMF) (99.8%, Aldrich, Sureseal[®]), acrylic acid (AA) (glacial, monomer grade), acrylic acid-1-¹³C [98% chemical purity stabilized with 1000 ppm hydroquinone (HQ), 99% isotopic purity, Isotec, Inc.), trimethylolpropane (TMP) (99+%; recrystallized, Aldrich), oxalyl chlo-

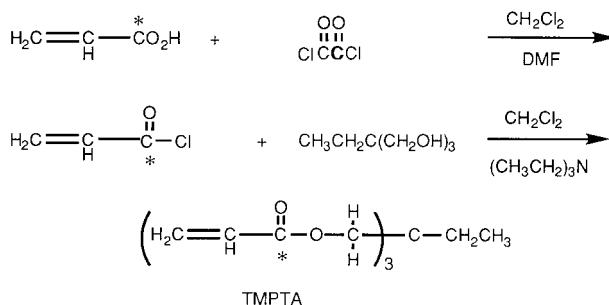


Figure 3 Synthetic procedure for preparation of a ¹³C-labeled crosslinker.

ride (OC) (99+%, Aldrich), sodium carbonate (Fischer, certified A.C.S.), and sodium persulfate (98+%, Aldrich).

Preparation of ^{13}C -Labeled TMPTA

The reaction was conducted, under N_2 , in an oven-dried 100-mL three-necked flask equipped with a magnetic stir bar, an N_2 line (attached to a bubbler), an addition funnel with a pressure-equalizing side arm, and a septum. The flask, further dried with a heat-gun under positive N_2 flow, was charged with acrylic acid- $1\text{-}^{13}\text{C}$ (0.975 g, 0.0135 mol), DMF (0.20 g), and CH_2Cl_2 (5 mL). To the stirred colorless solution at 0°C was added dropwise, oxalyl chloride (1.718 g, 0.0133 mol) in CH_2Cl_2 (5 mL) over a 20-min period. The resulting clear colorless solution was stirred at ambient temperature for 2 h. The solution was again cooled to 0°C and a solution of TMP (0.549 g, 0.00409 mol), ET_3N (3.187 g), and CH_2Cl_2 (10 mL) was added over a period of 30 min. The bright yellow mixture that formed was allowed to stir at 0°C for 2 h, then at room temperature for 30 min and then the reaction mixture was quenched by dropwise addition of 20 mL of deionized water. To the resultant two-phase mixture was added 0.00036 g of monomethyl ether of hydroquinone (MEHQ) (300 ppm) and of 0.00024 g HQ, (200 ppm) and the two phases were separated and the CH_2Cl_2 layer washed successively as follows: water (2×40 mL), 5% aqueous HCl (2×40 mL), saturated aqueous NaHCO_3 (40 mL), and brine (40 mL). To the resulting yellow solution was added an additional quantity of MEHQ (0.00036 g, 300 ppm) and HQ (0.00024 g, 200 ppm), and the solution was dried (Na_2SO_4). The mixture was filtered and concentrated on a rotary evaporator at room temperature to give 1.21 g (100%) of a light amber oil. The product was stored in the freezer after flushing the container with air. HPLC showed the crude product to consist of three major peaks (plus antioxidant peak) and several minor peaks. The major component was the trivinyl TMPTA, which was isolated by preparative HPLC on a 25×2 cm Hypersil ODS, 52 μm column using an 80/20 mixture of methanol/water containing 0.01% formic acid, to yield 0.53 g (43%) of a 95+% pure product.

Preparation of Polymerization Feed Mixtures

A mixture of ^{13}C -labeled trimethylolpropane triacrylate (3.6 wt %) in glacial acrylic acid was pre-

pared from the purified crosslinker and kept frozen until immediately before use. The crosslinker solution was diluted with additional acrylic acid to adjust the level of crosslinker, and a sodium persulfate stock solution added to the acid solution to provide the initiator and adjust the solids level. The concentration of initiator was varied by the concentration of the sodium persulfate in the stock solution. A typical feed mixture, at 0% neutralization and 36.4% solids, containing 1.00% of the ^{13}C -TMPTA and 600 ppm sodium persulfate (BOAA) was prepared by combining 1.111 g of the ^{13}C -TMPTA stock solution (3.6 wt %) in acrylic acid, 2.889 g of glacial acrylic acid, and 7.000 g of a sodium persulfate stock solution (0.0343% in DI water). When preneutralized feed mixtures were prepared, anhydrous sodium carbonate was added (slowly with stirring) directly to the diluted feed mixture. Most of the polymerizations were conducted at percent solids or percent neutralizations where the crosslinker was totally miscible in the reaction mixture. One feed mixture was prepared at 65% neutralization and 30% solids with 1.0% ^{13}C -TMPTA. This exceeded the solubility limits of TMPTA and the crosslinker was dispersed with polyvinyl alcohol following the procedure of Prud'homme et al.⁷

In the feed mixtures containing the labeled crosslinker, the intensity of the TMPTA carbonyl peak at 164.5 ppm in the NMR (Fig. 4) was enhanced, relative to that of acrylic acid at 166.8 ppm, to the point where the resulting decrease in both during polymerization could be easily observed. Samples were polymerized to low and high conversion and the amount of uncrosslinked polymer determined as well. The extractable polymer was quantified by the method of Cutié et al. using 0.9% NaCl extraction and HPLC analysis.²⁸

NMR Kinetic Analysis

An NMR technique was used to monitor the polymerization rates *in situ*. This method made it possible to obtain isothermal data during exothermic conditions of up to 2% conversion/min in 5 mm tubes. The 5 mm diameter NMR tubes were loaded via a glass pipette and deoxygenated with nitrogen. The tubes were deoxygenated for a minimum of 60 min. After the deoxygenation, the cap was sealed and the sample was sonicated (20–30 s) to remove the nitrogen gas from the saturated liquid so that bubbles did not form in the sample as it polymerized. (Bubbles give rise to severe line broadening in the ^{13}C NMR spectra, dramatically

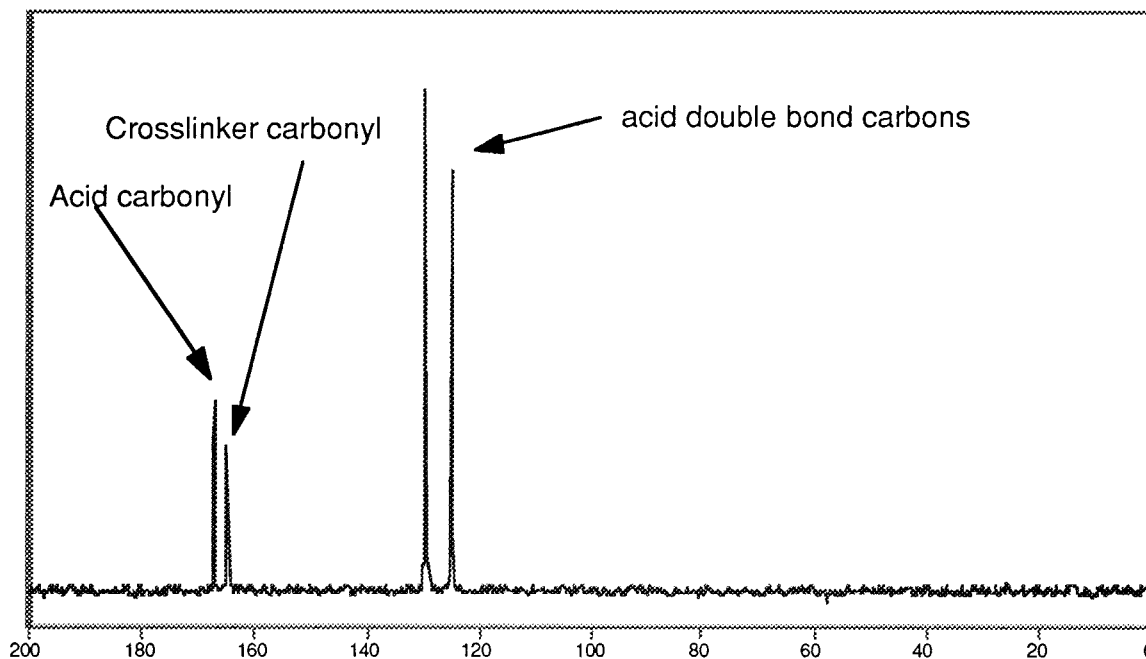


Figure 4 Typical feed mixture of acrylic acid and 1.0 wt % ^{13}C -labeled TMPTA in water at 20% solids.

degrading their quality.) The sample was then placed in the temperature-equilibrated, nitrogen-filled probe of the NMR spectrometer and data were acquired. The time of data accumulation for each spectrum was determined by the number of scans and the delay time between scans. A typical series of ^{13}C NMR spectra, from low to high conversion, are given in Figure 5. The crosslinker conversion was determined from the area of the TMPTA carbonyl resonance at 164.5 ppm and the incorporated TMPTA carbonyl resonance at 174 ppm, while the acrylic acid conversion was determined from the area for the olefinic carbons of acrylic acid at 130 and 124 ppm and the incorporated acrylic acid backbone carbon resonances at 33 and 40 ppm.

The resonances used above for quantitation were chosen because the carbonyl resonances possessed very long spin lattice relaxation times, T_1 . For example, the acrylic acid carbonyl resonance had a T_1 value of 34 s in a 20% solution in water at 30°C and at 60°C the T_1 was greater than 40 s. Therefore, the vinyl carbons of acrylic acid, whose T_1 values were almost a factor of 10 faster, were utilized for quantitative purposes.

To detect the TMPTA at about 0.5 wt % so as to quantify its incorporation, it had to be ^{13}C en-

riched. The natural abundance of ^{13}C is 1%, thus enriching the carbonyl carbon with 99.8% ^{13}C allowed for a 100-fold increase in sensitivity. There was only one reasonable choice for a carbon on the molecule to label that could be assured of no interferences from the acrylic acid carbon resonance, namely the carbonyl. The T_1 value of the TMPTA carbonyl as a 50% solution in methanol at 30°C was 14 s. Obviously, this value would lengthen somewhat at elevated temperatures. Therefore, the choice of acquisition parameters for the NMR experiment involved a compromise between accuracy and signal to noise (S/N). The conditions chosen utilized a 10 s delay between pulses with a 45° pulse width. These conditions were quantitative within the precision of the experiment (which was, in reality, determined by the S/N).

The temperature of the probe was set to within $\pm 1^\circ\text{C}$ using ethylene glycol as an internal reference, the ^1H -NMR chemical shift difference between the methylene and hydroxyl protons of ethylene glycol giving an accurate measure of temperature. Because the polymerization was exothermic, the sample temperature was found to increase above the NMR set point when the rate of reaction exceeded about 2% per minute for sam-

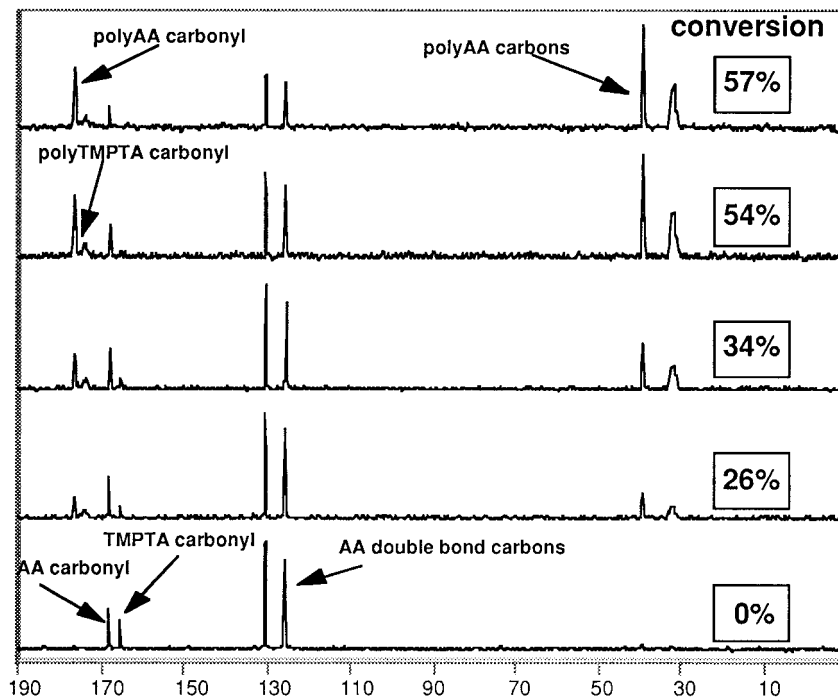


Figure 5 ^{13}C NMR spectra of the 55°C polymerization of acrylic acid containing 1.0% (weight) ^{13}C -labeled TMPTA.

ples at 30% solids or higher in 5 mm NMR tubes. This was partly due to the limitations of heat transfer from within the sample to the NMR tube but mostly to the ability to transfer the heat from the NMR tube within the NMR probe. The temperature within the NMR probe was maintained by temperature equilibrated nitrogen gas that was forced around the sample. The heat transfer characteristics of the gas were not sufficient to manage the large exotherms in the sample. Therefore, the reaction rates were kept below 2% per minute.

The ^{13}C NMR spectra were obtained at 75.4 MHz using a Bruker AC-300 NMR spectrometer, model number HO2129-ECL-24, S/N 0898. The data acquisition parameters utilized were as follows: pulse width = 45° , delay time = 9.5 s, size = 16 K, accumulation time = 0.41 s, sweep width = 20 kHz, apodisation = exponential, 5 Hz broadening, decoupling = complete.

In order to obtain good data for the reactivity ratio r_2 , a polymerization containing a high concentration of TMPTA was conducted. The solubility of TMPTA at high levels was investigated in order to select a mixture that was one phase. Only unneutralized mixtures were investigated be-

cause of the limited miscibility of water, TMPTA, and acrylic acid at high TMPTA concentrations (25–50%) and neutralization only makes it worse. A composition containing 66.6% solids and a TMPTA to acrylic acid ratio of 1/3 was found to be a one-phase system and was selected for the NMR polymerization. A sample of pure trifunctional TMPTA prepared in the laboratory was used for the polymerization. Commercial TMPTA is a mixture of more than 10 components, of which the trivinyl component is less than 60%. The ^{13}C -NMR spectrum of the TMPTA used in the polymerization is shown in Figure 6. The mixture was polymerized at 70°C and the relative rate of decrease of TMPTA was used to derive r_2 while fixing r_1 at 0.49.

Experimental Design

The variables that were investigated for effects on the reactivity ratios include: percent neutralization (0, 25, 50, and 65%), temperature (55 , 70 , and 80°C), percent solids (20–28% for 0% neutralized and 30–42% for 65% neutralized), and one-phase vs. two-phase (dispersed with polyvinyl alcohol) crosslinker systems.

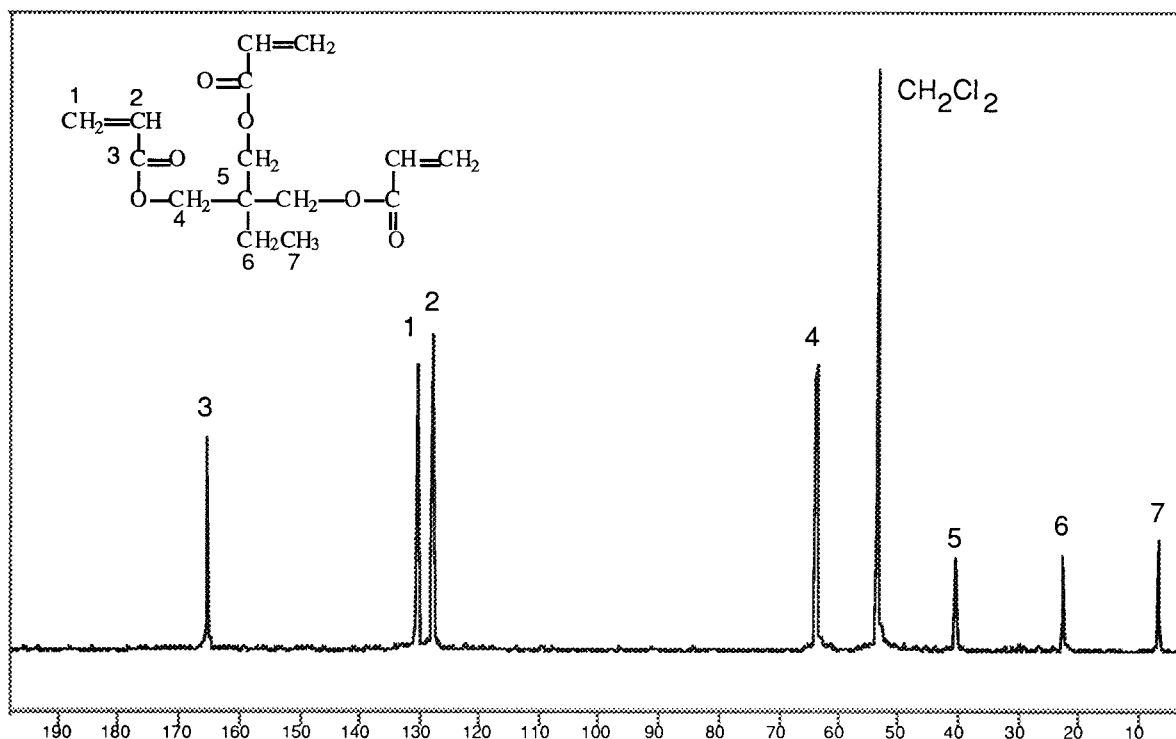


Figure 6 Carbon NMR spectrum of a TMPTA crosslinker with methylene chloride internal reference.

Method to Determine r_1 and r_2

The SimuSolvTM simulation and optimization program was used to determine the reactivity ratios from the composition profile data. When molar monomer conversion (x) is used as the independent variable, then monomer (f) and polymer (F) composition profiles depend only on the reactivity ratios (r) and initial conditions (f_o). Thus, r_1 and r_2 can be varied until an optimal fit is acquired.²⁹ As the reactivity ratios were fit, it was observed that the profiles were insensitive to r_2 . The insensitivity can be explained by the low levels of crosslinker functional groups ($f_2 \ll 1$) and their preferential incorporation into the polymer ($r_1 < 1$). The well-known copolymer composition equation reduces to the following as the crosslinker mol fraction approaches zero, where F_2^* is the instantaneous molar incorporation of crosslinker functional groups.

$$F_2^* = \frac{f_2}{r_1} \quad f_1 + f_2 = 1 \quad F_2^* + F_1^* = 1$$

The composition balances are very easy to inte-

grate at these low levels of crosslinker. The monomer composition profile vs. molar monomer conversion (x) is given below, where f_{2o} is the initial molar composition fraction of crosslinker functional groups. An overall mass balance is used to calculate polymer composition (F_2), which is the molar fraction of reacted crosslinker functional groups.

$$f_2 = f_{2o}(1-x)^{(1-r_1)/r_1} \quad F_2 = \frac{f_{2o} - (1-x)f_2}{x}$$

RESULTS

The rate of incorporation of the crosslinker (TMPTA) was much more rapid under all conditions than the rate of polymerization of acrylic acid. The rate of incorporation of crosslinker, resulting in earlier depletion from the monomer mixture, was faster in the more neutralized systems. At 55°C and 65% neutralization, the crosslinker was below the NMR detection limits (ca. 0.01% based on acrylic acid) at 70% conversion of

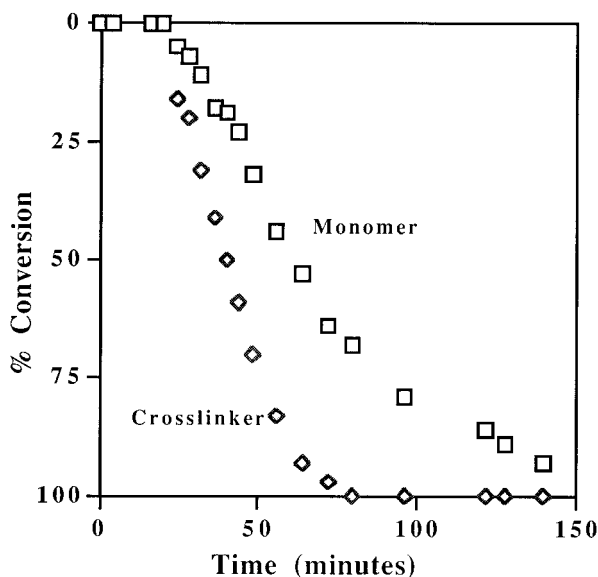


Figure 7 Rate of incorporation of TMPTA into polyacrylic acid (65% neutralized) polymerized at 42% solids (600 ppm sodium persulfate based on acrylic acid) at 55°C.

the acrylic acid (Fig. 7). A similar but slower rate of incorporation was seen at 0% neutralization.

It was also observed during the copolymerization of acrylic acid and the ^{13}C -labeled crosslinker that all of the double bonds from the crosslinker (TMPTA) reacted and not just two, as previously proposed. From the narrow line widths of the pendant double bonds and a lack of chemical shift (from the original TMPTA position) when pendant, it was concluded that significant mobility exists for the pendant groups and steric hindrance for reaction is not a problem. Once incorporated into the polymer chain, some reduction in mobility at the crosslink site appears to be present, based on the slight broadening of the saturated ester carbonyl peaks from the ^{13}C -crosslinker at 174 ppm (carbonyl groups adjacent to incorporated double bonds). This lack of change of the NMR chemical shift for the pendant double bonds simplified the analysis, but, unfortunately, did not allow the determination of the reactivity ratio of the second and third double bonds. However, based on the continued rapid rate of incorporation and significant mobility of the pendant groups, little change in reactivity ratio is believed to occur. Because of this, we have treated the various double bonds of TMPTA as a single entity and

have calculated a single reactivity ratio that applies to all three double bonds.

The reactivity ratio r_1 as deduced from fitting the data with the SimuSolv[®] model, decreases from 0.77 at 0% neutralization to 0.31 at 65% neutralization (Table II). This is consistent with the trends discussed previously for various acrylic acid copolymers upon neutralization. As the species in the mixture are ionized, the growing polyelectrolyte chain prefers to attack the unionized crosslinker. From our data and monitoring technique we cannot rule out rapid incorporation of the pendant double bonds through intramolecular cyclization, but the cited references describing conditions that favor it suggest that it is not a major pathway for reaction at these high solids conditions and low crosslinker levels.

Temperature normally has very little effect on reactivity ratios and this was also observed in this study between 55–80°C for 65% neutralized acrylic acid (Table II). The reactivity ratio only increased from 0.31 to 0.35 over this temperature range. For 0% neutralization, the reactivity ratio increased from 0.44 to 0.77 when the solids were increased from 20 to 36%. This can be viewed as a solvent effect. From the high TMPTA ratio experiment, r_2 was determined to be 3.6.

The composition of the 65% neutralized acrylic acid feed mixture and polymer was compared to that predicted using the integrated form of the copolymerization equation using the measured value of $r_1 = 0.31$ (Fig. 8). An excellent fit of the data is obtained throughout the entire conversion range with the use of the single reactivity ratio. This is consistent with the pendant double bonds having the same (similar) reactivity as the initial crosslinker.

From the above data it is clear that acrylate crosslinkers are rapidly incorporated into the gel at a disproportionate rate at the beginning of the polymerization. Because the molecular weight of the polyacrylic acid decreases with conversion as the acrylic acid is depleted according to $M_n \alpha k_p [M]^w \left(\frac{fk_d [I]}{k_t} \right)^{0.5}$, the polymer chains made late in the polymerization are less likely to be incorporated into the network through a crosslinker double bond. Samples of 65% neutralized polyacrylic acid were prepared isothermally at 55°C at 34% solids using 1600 ppm (based on acrylic acid) sodium persulfate as the initiator and the molecular weight determined by the method of Cutié (Fig. 9).³⁰ The cumulative molec-

Table II Reactivity Ratios Determined by NMR for Acrylic Acid and ^{13}C -Labeled TMPTA under Varied Conditions

| Temperature (°C) | Percent Neutralization | [Solids] Percent | [TMPTA] wt % | r_1 | r_2 | Solvent |
|------------------|------------------------|------------------|-----------------|-------------------|---------------|--------------------------|
| 55 | 0 | 36 | 1.0 | 0.77 ± 0.02 | | water |
| 55 | 25 | 38 | 1.0 | 0.49 ± 0.02 | | water |
| 55 | 65 | 42 | 1.0 | 0.31 ± 0.01 | | water |
| 55 | 0 | 20 | 1.0 | 0.44 ± 0.02 | | water |
| 55 | 25 | 35.6 | 0.5 | 0.47 ± 0.01 | | water |
| 70 | 65 | 42 | 1.0 | 0.33 ± 0.01 | | water |
| 80 | 65 | 42 | 1.0 | 0.35 ± 0.02 | | water |
| 55 | 0 | 20 | 1.0 | 0.42 ± 0.02 | | water |
| 70 | 0 | 20 | 1.0 | 0.49 ± 0.01 | | water |
| 70 | 0 | 66.6 | 25 ^b | 0.49 ^c | 3.6 ± 0.6 | water |
| 55 | 0 | 20 | 1.0 | 0.40 ± 0.01 | | acetic acid ^a |
| 70 | 0 | 28 | 0.635 | 0.49 ± 0.01 | | acetic acid ^a |
| 70 | 0 | 20 | 1.0 | 0.49 ± 0.01 | | acetic acid ^a |
| 85 | 0 | 20 | 1.0 | 0.85 ± 0.08 | | acetic acid ^a |

^a 75/25 (w/w) acetic acid/water used as solvent.

^b Used pure trifunctional TMPTA.

^c r_1 was fixed at 0.49.

ular weight decreases from several million to about 400,000 at 90% conversion. Very low molecular weight is made at high conversion.

Using the reactivity ratio, $r_1 = 0.31$, as determined for the polymerization of 65% neutralized acrylic acid with TMPTA and feed composition, the average instantaneous distance between crosslinks can be predicted for the network. The plot in Figure 10 for the 65% neutralized acrylic polymerization shows that for the 0.5% TMPTA case, initial polymer chains formed will have an M_n between crosslinks of about 5500 g/mol. This means that there will be an average of one cross-

link every 76 monomer units. If we assume that the number average molecular weight of the initial polymer chains is 5,000,000 g/mol, there will be 65,790 crosslinks in each molecule. However, because of the rapid depletion of the crosslinker, at 90% conversion, the distance between crosslinks will be 1,000,000 g/mol. This is much greater than the M_n being formed at this point in the polymerization and the number of crosslinks per chain is much less than 1. Potentially, improved

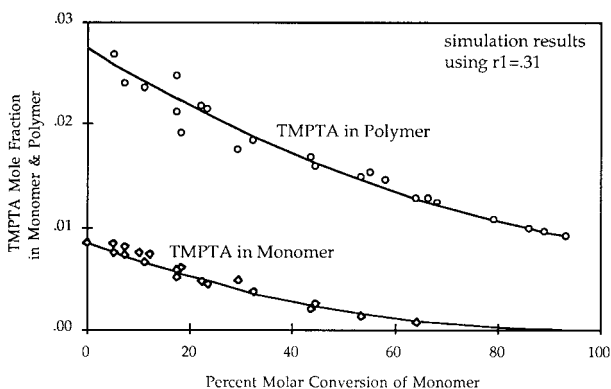


Figure 8 TMPTA content for the monomer mixture and polymer vs. conversion using $r_1 = 0.31$ (for 65% neutralization); predicted (lines) and experimental results (circles and squares).

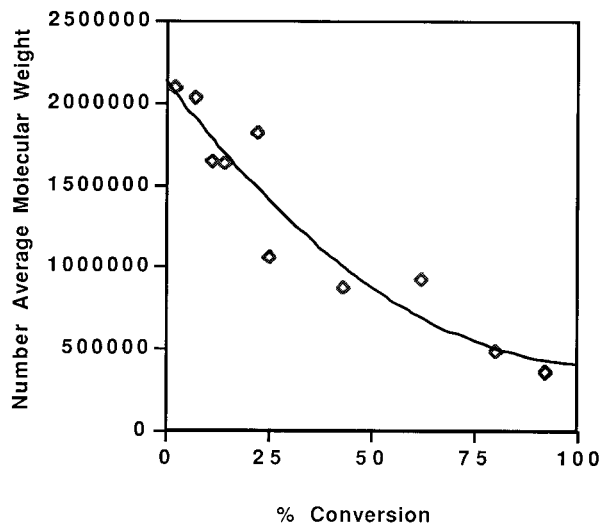


Figure 9 Effect of conversion on the cumulative number average molecular weight of 65% neutralized polyacrylic acid prepared isothermally at 55°C.

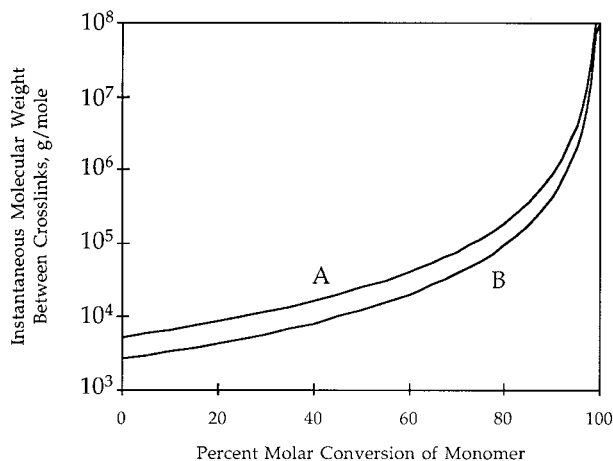


Figure 10 Predicted instantaneous distance between crosslinks in polyacrylic acid based on $r_1 = 0.31$ (for 65% neutralized conditions) prepared from a feed composition containing (A) 0.50% (weight) TMPTA and (B) 1.00% (weight) TMPTA.

superabsorbents could be prepared by use of a crosslinker that is more uniformly incorporated. The higher r_1 value for the polymerization of unneutralized acrylic acid and TMPTA results in a slower rate of incorporation of the crosslinker, leaving it more available for reaction later in the polymerization (Fig. 11).

The lack of crosslinker in the polymer chains formed late in the polymerization should lead to soluble polymer. However, very low levels of extractables (<1.0%) were found in the samples polymerized under conditions where TMPTA was totally soluble in the feed mixture. This included the unneutralized samples at 20–36% solids and the samples prepared at 42% solids with 65% neutralization. Samples prepared at 30% solids and 65% neutralization, however, had very high levels of extractables compared to the other samples (3.9% at 55°C, 9.0% at 70°C, and 22.5% at 80°C). Under the conditions of high neutralization and lower % solids, TMPTA was only partially soluble in the reaction mixture, which resulted in a two-phase system. Even though polyvinyl alcohol was used as a dispersion aid, the TMPTA was observed by ^{13}C -NMR to disappear more rapidly than in the miscible systems, which resulted in an “apparent” r_1 of about 0.2. By 50% conversion the ^{13}C -TMPTA was below the detection limits of the NMR and it appeared that the dispersed TMPTA did not redissolve and become copolymerized into the network. Because the acrylic acid in the mixture is the solvent for the TMPTA, conversion of it to polymer should make the TMPTA less

soluble in the reaction mixture, consistent with our observations. The low effective incorporation of TMPTA into the network and not the reactivity of the third double bond appears to be the cause of the lower modulus gels made under these conditions.

Based on the fact that very low levels of extractables are generated in these polymerization reactions and the fact that the crosslinker was essentially depleted by about 70% conversion, the polymer formed toward the end of the polymerization must be bound to the crosslinked gel by other than a “normal” crosslinking mechanism. Covalent grafting is the most likely mechanism.

Grafting of polymer, onto a pre-formed polymer is well known in emulsion, suspension, and solution polymerizations.³¹ Organic azo compounds, such as AIBN and Wako V-50, are known to be much less effective in hydrogen abstraction and, thus, result in much lower efficiency of grafting.³² Factors such as temperature, monomer to pre-formed polymer ratio, initiator level, and the presence of other chain transfer agents affect the amount of graft formed. In a water phase acrylic acid, adiabatic polymerization process, grafting would be expected to become more pronounced toward the end of the polymerization as the temperature rises to the peak and the ratio of polymer to monomer increases. Sodium persulfate is an excellent grafting initiator and will abstract hydrogen atoms from a variety of polymer species. Tobita has addressed the issue of chain transfer to polymer in both emulsion and solution pro-

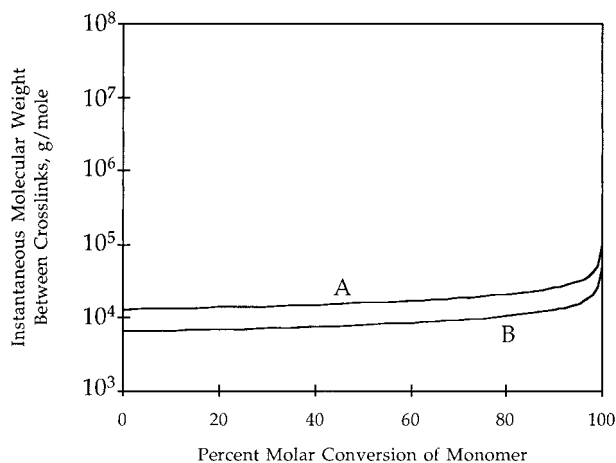


Figure 11 Predicted instantaneous distance between crosslinks in polyacrylic acid based on $r_1 = 0.77$ (for unneutralized conditions) prepared from a feed composition containing (A) 0.50% (weight) TMPTA and (B) 1.00% (weight) TMPTA.

cesses.³³ Grafting is believed to occur at high conversion in solution processes while in emulsion processes, some grafting occurs even at low conversion. In a solution process, the high concentration of polymer and low concentration of monomer at the end of the process, favor grafting. Our model of a inhomogeneous crosslinked network in a crosslinked acrylic acid process resulting from the high reactivity of the crosslinker is consistent with Tobita and Hamielec's modeling of the crosslinked system of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM).³⁴ They believed that the bulk polymerized MMA/EGDM copolymer was inhomogeneous on a microscopic scale.

CONCLUSIONS

The relative rate of incorporation of acrylate crosslinkers into polyacrylic acid gels was exceedingly rapid. When acrylic acid was partially neutralized (65%), the crosslinker was totally polymerized by 70% conversion of the acrylic acid. The relative rate of copolymerization of the crosslinker was slower when the acrylic acid was not preneutralized, but still rapid. The reactivity ratio, r_1 , varied from 0.31 (65% neutralization) to 0.77 (unneutralized). The reactivity ratio was affected by the % solids (solvent effect), but insensitive to temperature over the range of 55–80°C. It was observed that all of the double bonds of TMPTA were incorporated into gel network as opposed to prior models of only two bonds reacting. The reported inefficiency of TMPTA (2/3 effective) is postulated to be caused by a solubility problem in the monomer mixture at high percent neutralization and lower percent solids.

Superabsorbent polymer gels prepared with acrylate crosslinkers such as TMPTA, consist of a very heterogeneously crosslinked network of highly crosslinked, high molecular weight polyacrylic acid formed during the early stages of the polymerization, lower molecular weight chains that form during the middle of the polymerization bridging through the pendant vinyl groups and containing a greater distance between crosslinker sites than chains formed initially and grafted polymer formed (especially) toward the end of the polymerization. It appears that 30% or more of the polymer chains are attached to the network via grafting. Gels formed under partially neutralized conditions are more heterogenous than those prepared using unneutralized conditions.

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