

Mechanical Stability of Trimethylolpropane Trimethacrylate-Based Polymers

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SYNOPSIS

Trimethylolpropane trimethacrylate (TRIM) was homopolymerized and copolymerized with methyl methacrylate (MMA), glycidyl methacrylate (GMA), and acrylamide (AA), respectively, in various solvents and at various temperatures. For comparison, poly(styrene-*co*-divinyl benzene) [poly(S-*co*-DVB)] gels were selected. The mechanical stability was measured by compression of the swollen gels. The porogen served as swelling agent. The compression moduli increased with increasing TRIM concentration in the polymerization. The compression moduli of poly(TRIM) could be increased by copolymerization with low concentrations of comonomer. Low polymerization temperature decreased the mechanical strength of poly(TRIM). A good solvent increased the compression modulus. TRIM-based gels were at least as mechanically stable as were poly(S-*co*-DVB) gels.

INTRODUCTION

Porous materials used as the stationary phase in high-performance size-exclusion chromatography (HPSEC) should be mechanically stable. To achieve fast separation, high flow rates through the column are necessary. Because an increase in flow rate increases the pressure drop over the column, a compromise among particle size, flow rate, and mechanical stability of the gel structure is necessary.

Conventional polymer materials used as the stationary phase in SEC and HPSEC based on dextran,¹ acrylamide-bisacrylamide,^{2,3} and agarose show good separation properties at low flow rates. Styrene-*co*-divinyl benzene-based gels^{4,5} have much better mechanical stability. Each material has an optimal flow rate vs. pressure drop curve that depends on the particle size. Above a certain flow rate, the pressure increases asymptotically and the column material "collapses." This is due to deformation of the gel particles and "plugging" of the void spaces.

The mechanical properties of porous materials has been investigated by the resonance method⁶⁻⁸ (dynamic mechanical measurements) and by

compression measurements.⁹⁻¹¹ Porous materials based on trimethylolpropane trimethacrylate (TRIM) have been shown to have good separation properties in toluene.¹²⁻¹⁴ In this paper, the mechanical stability of the TRIM-based gels is reported. The compression moduli as a function of monomer/comonomer concentration is discussed. For comparison, poly(styrene-*co*-divinyl benzene) [poly(S-*co*-DVB)] gels were selected.

EXPERIMENTAL

Pretreatment

The monomers trimethylolpropane trimethacrylate (TRIM) (technical quality containing more than 98% TRIM, Merck), methyl methacrylate (MMA), (pure, Fluka), glycidyl methacrylate (GMA), (technical quality, Fluka), styrene (S) (pure, Merck), and divinyl benzene (DVB) (60% isomers and 35% ethyl vinyl benzene, Merck) were passed through a column of basic aluminum oxide to remove inhibitors.

Polymerization

The monomers were dissolved in various porogens: toluene (maximum impurities 0.3%, Riedel-de

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Haen), ethyl acetate (maximum impurities 0.005% Pronalys analytical reagent), *p*-xylene (pure, Merck), and heptane (pure, Merck). The solution polymerizations were initiated with α, α' -azoisobutyronitrile (AIBN) (analytical grade, Fluka) after purging with nitrogen for 1 min. Cylindrical gel pieces were obtained after polymerization for 8 h in vials with rolled rims and flat bottoms (34×24 mm ϕ). For more information about the polymerization conditions, see Tables I–III.

Swelling

The glass vials were cracked and the polymer cylinders were swollen for 24 h in the porogen (see Table I). To see if swelling equilibrium has been obtained, the TRIM gels were additionally swollen in toluene for 105 days.

CHARACTERIZATION

The mechanical stability of the gels was tested by uniaxial compression (Lloyd T30 K Tensile Testing Machine). Maximum load was 1 kN and the compression speed was set to 50 mm min⁻¹. Figure 1 shows the hooks used for the compression of the gels.

Calculation

The constitutive equation for a linear elastic solid,

$$E = \frac{\sigma}{\epsilon} \quad (1)$$

where E is Young's modulus (N m⁻²), σ is tensile stress (N m⁻²), and ϵ is tensile strain, can be rewritten as

$$E_c = \frac{F}{\epsilon_i \cdot A} \quad (2)$$

where E_c is the compression modulus (N m⁻²), F is the load on the specimen (N), ϵ_i is the strain at initial load, and A is the cross-sectional area normal to the load direction (m²). An example of a curve after uniaxial compression of a cylindrical gel is given in Figure 2.

For calculation of the compression modulus, a tangent at the initial load is drawn to obtain ϵ_i :

$$\epsilon_i = \frac{h_0 - h_1}{h_0} \quad (3)$$

where h_1 is the height of the compressed specimen at initial load (m) and h_0 is the height of the specimen before compression (m):

$$h_0 - h_1 = \frac{(x_0 - x_1)v_c}{v_p} \quad (4)$$

where x_0 and x_1 are the x values of the tangent at load zero and $1 \cdot 10^3$ N, respectively, v_c is the compression speed (mm min⁻¹), and v_p is the pen speed of the plotter (mm min⁻¹).

Table I Composition of Poly(TRIM) and Poly(TRIM-co-MMA) Gels Prepared for Compression Tests

Total Monomer (vol %)	Monomer Composition (mol %)		Initiator AIBN (mg)	Porogen	Reaction Temp (°C)
	<u>TRIM</u>			Toluene	60
20	100		21		
30	100		21		
30	100		21		40
40	100		21		
50	100		21		
50	100		21		
	<u>TRIM</u>	<u>MMA</u>		Toluene	54
30	90	10	21		
	80	20	21		
	60	40	21		
	40	60	21		
	20	80	21		
	10	90	21		

Table II Composition of Poly(TRIM-co-GMA) Gels Prepared for Compression Measurements

Total Monomer (vol %)	Monomer Composition (mol %)		Porogen	Reaction Temp (°C)
	TRIM	GMA		
10	52	48	Toluene	60
20	61	39		
30	61	39		
40	62	38		
50	63	37		
70	62	38		
30	100	—	Toluene	60/70
	79	21		
	63	37		
	38	62		
	22	78		
	9	91		
30	100	—	<i>p</i> -Xylene	60
	62	38		
	37	63		
30	100	—	Heptane	60
	60	40		
	37	63		

At least three samples of each composition were measured. The content of the initiator were in all samples 1% (w/v) of the total monomer phase.

RESULTS AND DISCUSSION

Many of the conventional gels for packing in SEC columns are cross-linked with divinyl benzene (DVB). In the present paper, the mechanical sta-

bility of TRIM-based gels is compared with that of DVB-based gels. SEC separation results have already shown good mechanical properties of the poly(TRIM)-based gels.¹²⁻¹⁴ Since the porosity of the polymer gels is determined by the total monomer

Table III Composition of Poly(TRIM-co-AA), Poly(DVB), and Poly(S-DVB) Gels for Compression Measurements

Total Monomer (vol %)	Monomer Composition (mol %)		Initiator AIBN (mg)	Porogen	Reaction Temp (°C)
	TRIM	AA			
30	100	—	21	Ethyl acetate	54
30	90	10			
30	80	20			
30	70	30			
30	60	40			
30	55	45 ^a			
30	—	100	21	Toluene	60
	50	50			
	50	50			
			21	Heptane	

^a The solubility of AA in ethyl acetate limited further increase of AA concentration.

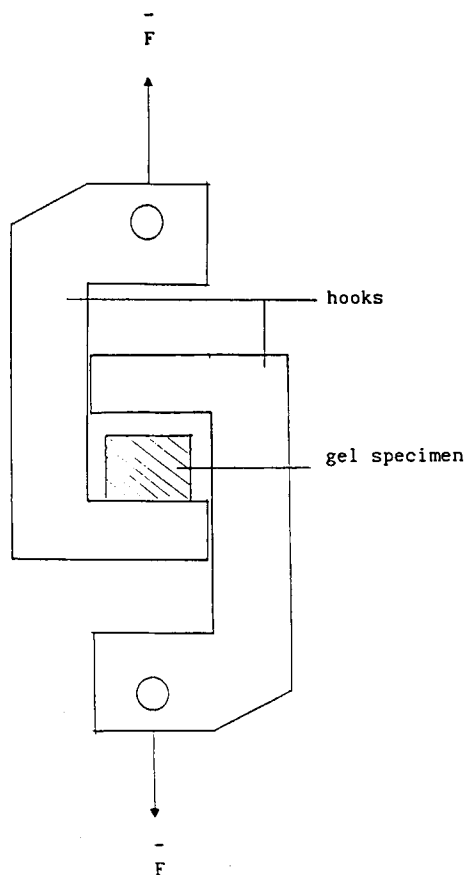


Figure 1 A schematic figure of the hooks used for the compression of the gels.

concentration, the mechanical stability of TRIM-based gels polymerized at various monomer and comonomer concentrations was studied.

The Effect of the Type and Amount of Monomers

Poly(TRIM)

The mechanical property of poly(TRIM) was studied by compression of toluene-swollen cylindrical gels. The results are based on at least three experiments for each concentration. The compression moduli increased with increasing concentration of monomer, as shown in Figure 3.

The compression modulus for poly(TRIM) (30 vol %) was found to be four times that of poly(DVB) (30 vol %) and slightly higher than poly(S-co-DVB) (30 vol %). Poly(TRIM) gels swollen in toluene for 105 days had the same values in compression moduli as those swollen for 24 h. Thus, 24 h were sufficient to reach swelling equilibrium.

Poly(TRIM-co-MMA)

The compression moduli for poly(TRIM-co-MMA) gels swollen in toluene decreased at high MMA concentrations, as shown in Figure 4. A maximum was observed at 10 mol % MMA. Poly(TRIM-co-MMA) gels containing 10 and 20 mol % MMA had higher compression moduli and strength than did poly(TRIM) gels (30 vol %).

With the assumption that the reactivity ratios are near unity, an explanation could be that the inner stresses in the gel decrease [compared to poly(TRIM)] because the number of degrees of freedom for the polymer chains increases. It results in decreased brittleness and increased toughness of the gels.

For gels containing 40–80 mol % MMA, the compression moduli were comparable to the one of poly(TRIM) (30 vol %, 60°C). The mechanical stability decreased as the MMA to TRIM ratio increased and the number of cross-linking points decreased. An increase in pores of diameters larger than 200 Å or larger with increasing MMA to TRIM ratio has been observed in the dry state (mercury porosimetry) and in SEC separation of polystyrene standards¹³ (swollen state). For gels of 90 mol % MMA, the compression moduli dropped to 2.0 MPa. They had lost their macroporosity and became rubberlike.

Poly(TRIM-co-GMA)

The dilution of TRIM with about 38 mol % GMA (based on total monomer content) did not seem to affect the compression moduli and strength, within the error of the measurements, compared to the compression moduli of poly(TRIM) gels. The compression moduli increased proportionally with the total monomer content (Figs. 3 and 5).

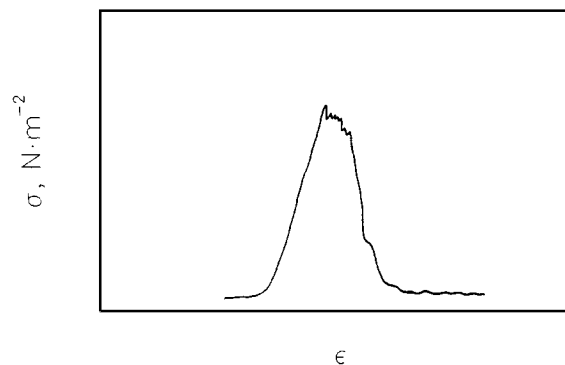


Figure 2 Stress-strain curve obtained during compression of a gel specimen.

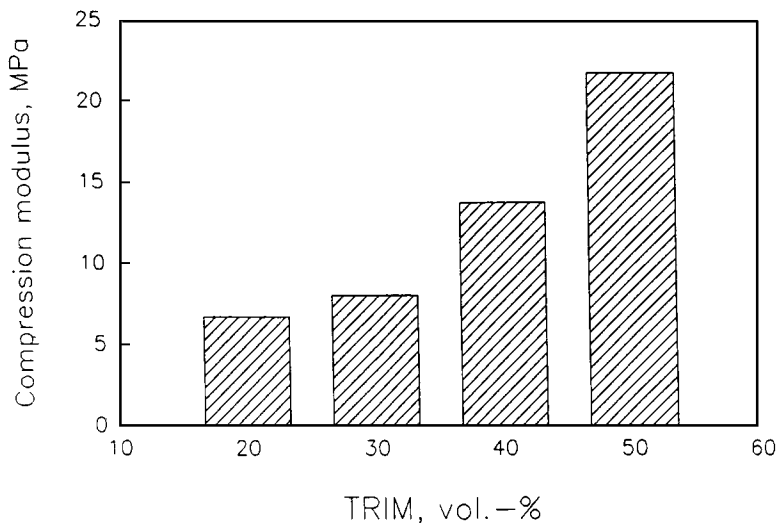


Figure 3 Compression moduli for poly(TRIM) gels at various monomer concentrations. The standard deviations of the values of compression moduli for poly(TRIM) 20, 30, 40, and 50 were 1.0, 2.9, 3.5, and 2.9, respectively.

Gels of poly(TRIM-*co*-GMA) containing less than 60 mol % GMA were tough although they fractured completely during the compression tests. Gels containing 60–90 mol % GMA fractured partly and a core of the sample was left that could be reswollen. Inhomogeneities can be suspected, due to temperature gradients after gelation as the samples could not be stirred during polymerization. However, similar inferior properties were also obtained for suspension-polymerized gels in SEC experiments of polystyrene standards in toluene. The columns de-

teriorated during the run due to compression of the beads.¹⁴ The conclusion is that these gels are inhomogeneous and partly tough and partly compressible. Those containing more than 90 mol % GMA did not fracture as they were compressed. The samples regained their shape after reswelling in the porogen. These results made it possible to divide the gels of poly(TRIM-*co*-GMA) into three groups:

1. Tough and permanently macroporous gels. Content of GMA: 0–60 mol %.

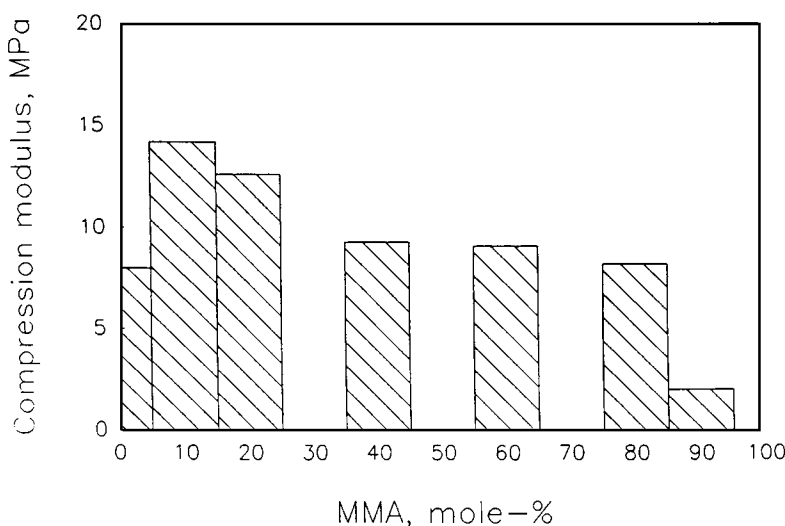


Figure 4 Compression moduli of poly(TRIM-*co*-MMA) gels. The standard deviations of the values of compression moduli of poly(TRIM-*co*-MMA) with 10, 20, 40, 60, 80, and 90 mol % MMA were 4.2, 0.7, 1.0, 0.9, and 0.1, respectively.

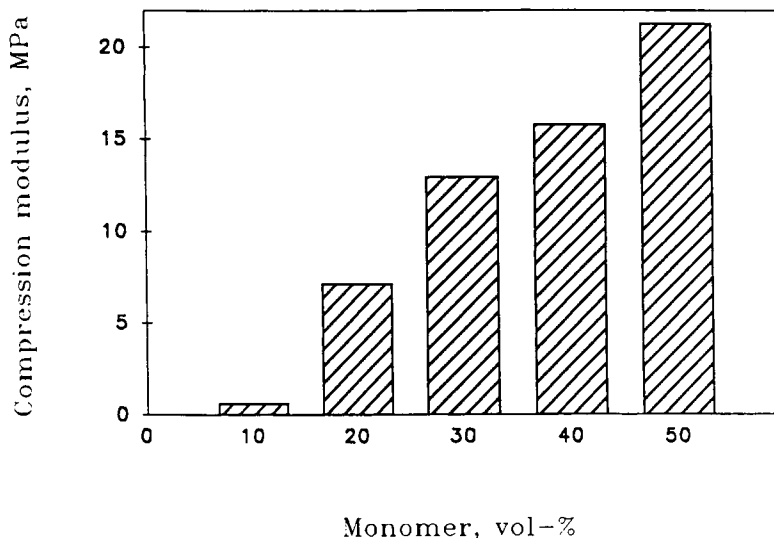


Figure 5 Compression moduli of poly(TRIM-co-GMA) gels containing 37 mol % of GMA. The standard deviations for gels with 10, 20, 30, 40, and 50 vol % of total monomer were 0.23, 2.49, 3.61, 3.04, and 1.52, respectively.

2. Partly tough and partly compressible gels. Content of GMA: 60–90 mol %.
3. Compressible and elastic gels. Content of GMA: 90–100 mol %.

Gels useful for HPSEC are generally found in the first group.

The compression moduli of copolymers of TRIM and GMA displayed a gradual decrease that resembled that of copolymers of TRIM and MMA. The ratio between total monomer and porogen was 30

vol % in all samples. The range of the compression moduli, as 10–80 mol % of either GMA or MMA was incorporated, was 8.5–10 MPa and 8.5–14 MPa, respectively. The main difference between the two series of gels was that poly(TRIM-co-GMA) gels did not display a maximum at low contents of GMA as did gels of poly(TRIM-co-MMA) (Figs. 4 and 6).

From porosity measurements in the dry state, we have observed an increase of larger pores ($r > 50$ Å) as the MMA concentration increased.¹³ Also in

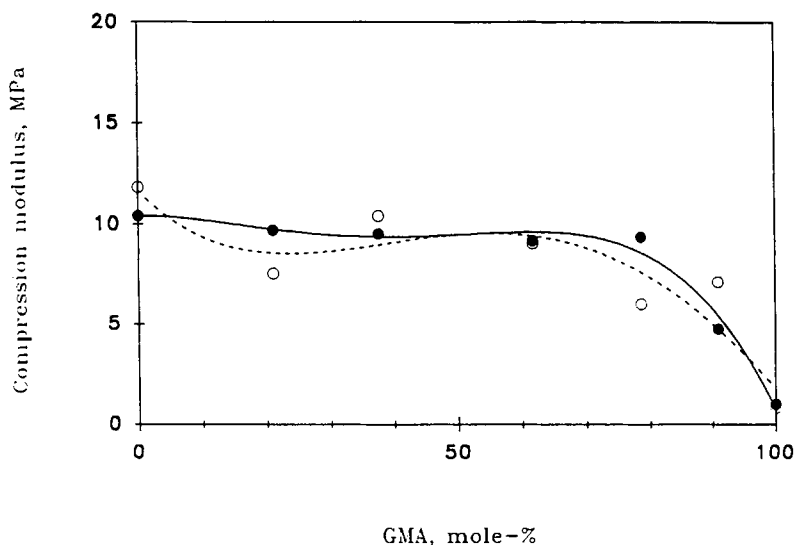


Figure 6 Compression moduli of poly(TRIM-co-GMA) gels where the ratio monomer to toluene was 30 vol %. The standard deviations for gels, containing 0, 21.05, 37.55, 61.6, 78.6, 90.89, and 100 mol % GMA, polymerized at 60°C (●—●) were 4.91, 2.50, 1.05, 2.77, 2.42, and 1.02, respectively. The standard deviations for gels polymerized at 70°C (○—○) were 2.26, 3.41, 2.69, 1.73, 1.05, 1.60, and 0.05, respectively.

the swollen state, the gels seem to have similar porosity. The separation volumes obtained for poly(TRIM-*co*-MMA) and poly(TRIM-*co*-GMA) after SEC separation of polystyrene standards in toluene were similar. The facts mentioned above are understandable in light of the similarity in reactivity ratios for TRIM-MMA and TRIM-GMA in toluene.

Poly(TRIM-*co*-AA)

The copolymerization of TRIM and acrylamide (AA) had to be performed in ethyl acetate due to poor solubility of AA in toluene. Poly(TRIM-*co*-AA) gels swollen in ethyl acetate showed an increase in compression moduli with increasing amounts of acrylamide in the gels, up to about 40 mol %. At higher AA contents, the mechanical stability decreased (Fig. 7).

Gels of 20 mol % acrylamide or less showed similar mechanical stability as poly(TRIM) (30 vol %, polymerized in ethyl acetate). The average compression moduli of gels containing 30 and 40 mol % were 12.3 and 13.6 MPa, respectively. Compared to the compression modulus of poly(TRIM) (30 vol %, polymerized in ethyl acetate), an increase of 35 and 49%, respectively, was observed.

A drop in compression modulus was observed as the amount of acrylamide was increased to 45 mol %. It is probably due to a higher elasticity of the basic gel structure caused by incorporation of acrylamide residues.

The mechanical stability remained fairly constant for the poly(TRIM-*co*-AA) gels. We assume another

type of copolymerization than for the above-mentioned systems. For copolymerization of AA with MMA in dioxane, reactivity ratios $r_{AA} = 2.39 \pm 0.32$ and $r_{MMA} = 2.44 \pm 0.38$ have been reported.¹⁵ It is reasonable to assume that r_{AA} and r_{TRIM} are greater than unity (and, therefore, also $r_{AA} \cdot r_{TRIM} > 1$), i.e., there is a tendency of block formation. The block length increases with increasing monomer concentration. For the tested TRIM/AA ratios, no collapse of the gel structure was observed.

Comparison

The mechanical stability of the different polymer gels is summarized in Figure 8. The compression modulus of poly(TRIM) was four times as high as that of poly(DVB). TRIM-based copolymers [i.e., poly(TRIM-MMA), poly(TRIM-GMA), and poly(TRIM-AA)] had better compression moduli than poly(S-*co*-DVB). The reason could be the better mechanical stability of poly(TRIM) and a decrease of the inner stresses in the network due to incorporation of comonomer.

Evidently, poly(DVB) developed still higher inner stresses since it had low modulus and was very brittle. Copolymerization caused a dramatic increase in modulus for the polymers (Fig. 8).

The Effect of the Porogen

The nature of the solvent seemed to play an important role for the mechanical stability of poly(TRIM-*co*-GMA) gels. It has been shown that the difference

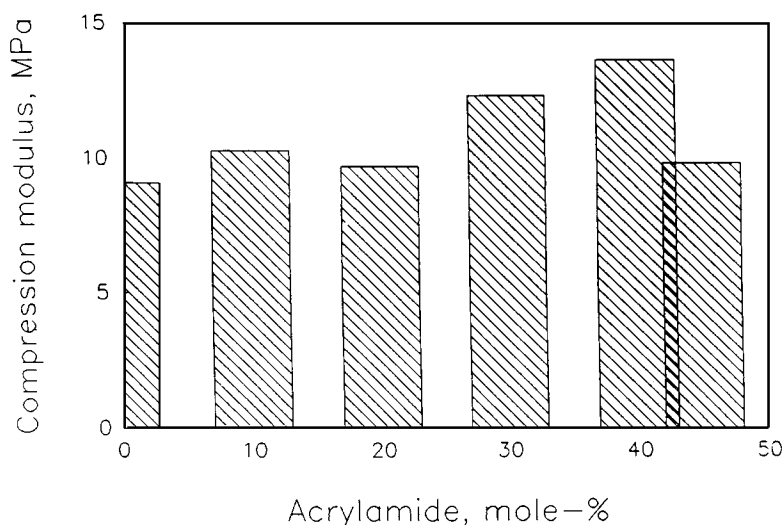


Figure 7 Compression moduli of poly(TRIM-*co*-AA) gels. The standard deviations of the values of compression moduli of poly(TRIM-*co*-AA) gels of 10, 20, 30, 40, and 45 mol % AA were 1.2, 3.7, 1.2, 0.2, and 1.1, respectively.

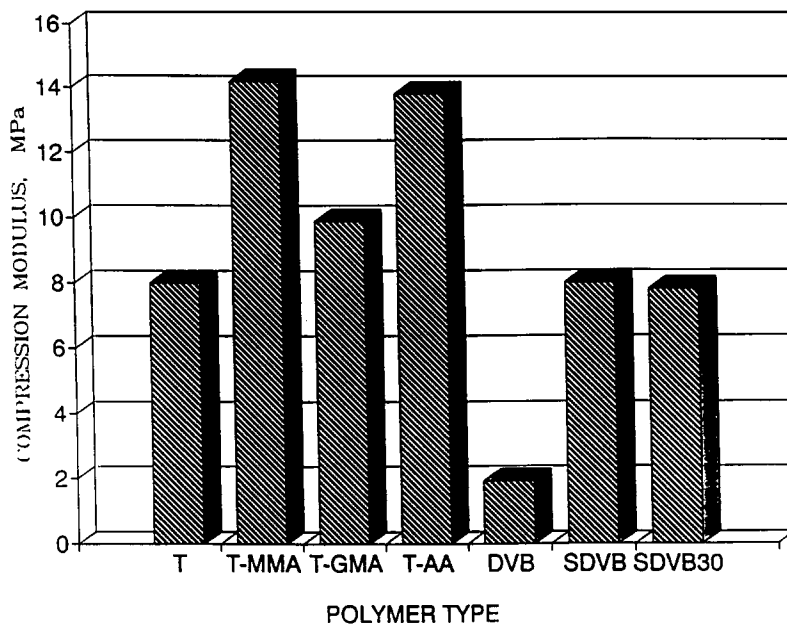


Figure 8 Comparison of compression moduli of TRIM-based gels with DVB-based gels: T, TRIM; SDVB, styrene-*co*-divinyl benzene (polymerized in toluene); SDVB30, styrene-*co*-divinyl benzene (polymerized in heptane).

between the solubility parameter of the polymer and the porogen ($|\delta_{\text{pol}} - \delta_{\text{sol}}|$) should not be greater than $2 \text{ MPa}^{1/2}$ to obtain maximum swelling.¹⁶ The highest swelling of poly(TRIM) gels was obtained with toluene ($\delta = 18.2 \text{ MPa}^{1/2}$). The calculated solubility parameter for poly(TRIM) and poly(GMA) according to Hoftyzer-van Krevelen¹⁷ was 16.4 and $17.6 \text{ MPa}^{1/2}$, respectively. With these facts in mind, gels of poly(TRIM) and poly(TRIM-*co*-GMA) gels were prepared in three different solvents: heptane ($\delta = 15.1 \text{ MPa}^{1/2}$), *p*-xylene ($\delta = 18.0 \text{ MPa}^{1/2}$), and toluene ($\delta = 18.2 \text{ MPa}^{1/2}$).¹⁶ Gels prepared in heptane were turbid and crumbled easily, whereas gels prepared in either *p*-xylene or toluene were harder and tougher. The average compression modulus for all gels polymerized in heptane was about 2 MPa. Both toluene and *p*-xylene are good solvents for poly(TRIM-*co*-GMA) gels. However, the compression modulus was 3–4 MPa higher for gels polymerized in *p*-xylene as compared to those polymerized in toluene (Fig. 9). Also, the pore-size distribution shifted toward larger pores if *p*-xylene was used as porogen.¹⁸ Thus, it appeared that *p*-xylene was a better solvent than toluene for poly(TRIM-*co*-GMA) gels.

Influence of Polymerization Temperature

The mechanical stability of poly(TRIM) 30 was not influenced by the decrease to 40°C in polymerization temperature (Fig. 10). Though a decrease of unreacted double bonds with increasing polymerization

temperature has been reported,¹⁹ an increase in mechanical stability could not be observed for the poly(TRIM) 30 gel.

The compression modulus for the poly(TRIM) 50 polymerized at 40°C decreased and appeared to be one-third of that of the poly(TRIM) 50 synthesized at 60°C (Fig. 10). Because of lower reaction temperature, fewer pendant double bonds have reacted¹⁹ and a gel with lower mechanical stability is obtained. By extrapolation in a plot of final time (t_f) vs. polymerization temperature,²⁰ the polymerization of TRIM at 40°C in toluene should be completed after 2.5 h.

The effect on the compression moduli of an increase of the polymerization temperature from 60 to 70°C was within the error of the experiments for poly(TRIM-*co*-GMA) (Fig. 6). The postpolymerization of the gels polymerized at 60°C had not quite finished after 10 h of polymerization and the samples were still somewhat sticky. The data on the compression moduli of gels polymerized at 70°C were scattered as the polymerization rate was higher and a temperature gradient in the polymer solution could have introduced minor inhomogeneities. These samples were nonsticky.

CONCLUSIONS

Poly(TRIM)

The compression moduli for poly(TRIM) gels increased with increasing monomer concentration.

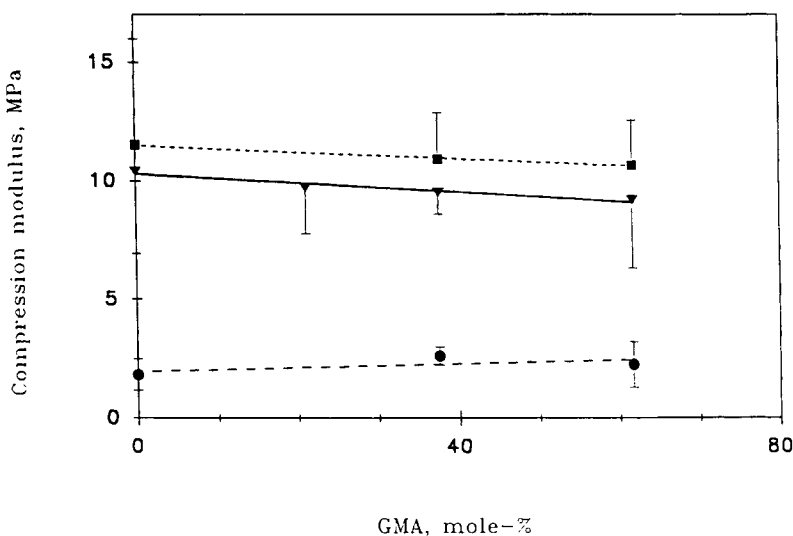


Figure 9 Poly(TRIM-co-GMA) gels polymerized in (●—●) heptane, (▼—▼) toluene, and (■—■) *p*-xylene.

High monomer concentration and low polymerization temperature resulted in poly(TRIM) gels of lower mechanical stability.

TRIM. Based on mechanical stability, poly(TRIM-co-MMA) gels containing up to 40 mol % MMA are suitable as HPSEC packing materials.

Poly(TRIM-co-MMA)

The compression moduli of poly(TRIM-co-MMA) increased for polymers with up to 20 mol % MMA incorporated and decreased at higher MMA content. The mechanical stability increased 75% [based on the compression modulus of poly(TRIM) 30] as 10 mol % MMA were copolymerized with 90 mol %

Poly(TRIM-co-GMA)

The compression moduli of gels containing 37 mol % of GMA increased from 0.5 to 20 MPa as the ratio total monomer to toluene increased from 10 to 50 vol %. Gels polymerized at 60 or 70°C showed similar compression moduli. Poly(TRIM-co-GMA) gels containing up to about 60 mol % GMA were suitable

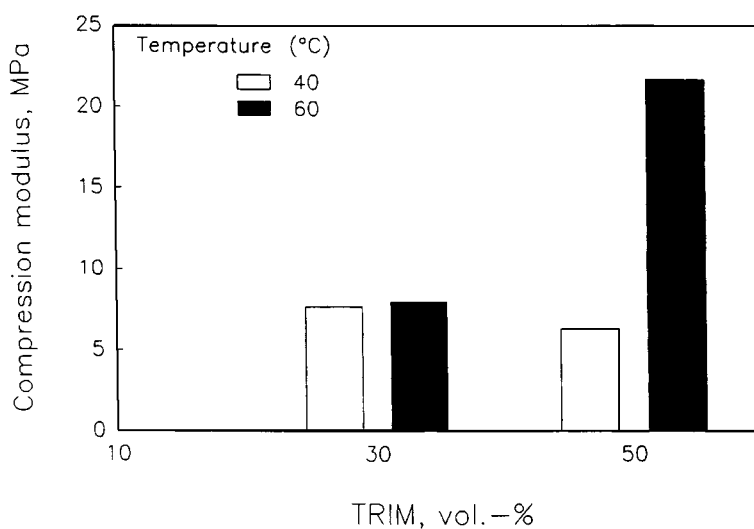


Figure 10 Compression moduli of poly(TRIM) gels obtained after polymerization at 40 and 60°C. The standard deviations of the values of compression moduli for poly(TRIM) 30 and 50, polymerized at 40°C, were 0.6 and 2.8, while for poly(TRIM) 30 and 50 polymerized at 60°C, the standard deviations were 2.9 for both gels.

for HPSEC. The smaller the difference between the solvent parameter (δ) of the gel and the porogen, the better the compression moduli and strength. *p*-Xylene gave higher compression moduli than did toluene. Heptane as porogen resulted in white, turbid gels that fractured easily.

Poly(TRIM-co-AA)

The mechanical stability of poly(TRIM-co-AA) increased for gels containing up to 40 mol % AA. The compression modulus of the gel consisting of 40 mol % AA was 49% higher than that of poly(TRIM) 30 (polymerized in ethyl acetate). Based on the mechanical stability, all tested poly(TRIM-co-AA) gels were suitable as HPSEC packing materials. Copolymerization of TRIM with MMA or acrylamide increases the mechanical strength at low comonomer concentrations.

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