Viscoelastic Behavior of Highly Crosslinked Poly(acrylic Acid)

A. R. GREENBERG and R. P. KUSY, *Dental Research Center, University of North Carolina, Chapel Hill, North Carolina 27514*

Synopsis

The effects of crosslinking upon the dynamic mechanical properties and swelling behavior of poly(acrylic acid) (PAA) have been studied. Materials were prepared by the free radical copolymerization of acrylic acid with varying amounts of the tetrafunctional monomer allyl acrylate (ALA). The results indicated a linear dependence of the glass-transition temperature (T_g) on composition, T_g increasing by ~43°C over the mole fraction range $X = 0$–0.37 ALA. Room temperature (25°C) modulus values, as determined by both dynamic and compression methods, were inversely proportional to the initial concentration of ALA. The degree of network formation has been characterized in terms of the molecular weight between crosslinks M_c, and the influence of this parameter on the swelling ratio was discussed.

INTRODUCTION

Recently, a poly(acrylic acid) (PAA)–alumina composite material has been utilized in orthopedic implant applications.[1] The successful use of this material depends upon crosslinking of the PAA matrix to control the physical and mechanical properties of the composite. Previous studies have shown that a network polymer can be obtained via acid anhydride formation.[2–6] For biomedical use, however, this method is undesirable because of the overlap of the anhydride and degradation reactions.[6] In the present investigation, crosslinking has been accomplished by the bulk copolymerization of acrylic acid (AA) with allyl acrylate (ALA). Divinyl monomers such as ethylene glycol dimethacrylate (EGDMA) have been used successfully to crosslink important biomedical polymers.[7] Although allyl acrylate differs from these materials in that the tetrafunctional allylic monomer has two double bonds of unequal reactivity, it has been demonstrated that the free radical polymerization of ALA and ALA–acrylic comonomers will produce insoluble, highly crosslinked polymers.[8–10]

A useful method for characterizing such systems is that of dynamic mechanical analysis. As the crosslink density is increased, the damping peak associated with the glass transition is shifted to higher temperatures, broadened, and decreased in magnitude.[11,12] The modulus above T_g is also highly dependent on the extent of network formation.[11–13] The dynamic mechanical properties of PAA,[14] PAA grafts,[14] and PAA copolymers[15] have been reported in the literature. PAA lightly crosslinked with ethylene dimethacrylate has been examined by Kolarik,[16] while Fitzgerald and Nielsen[17] investigated the viscoelastic properties of metallic salts of PAA. Recently, Mori et al.[18] reported on PAA–poly(oxyethylene) glycol (PEG) blends in which PAA was crosslinked by the reaction of the glycolic —OH groups with the pendant polyacid groups.

The primary purpose of the present investigation is to study the effects of high

degrees of main chain crosslinking on the dynamic mechanical properties of PAA. In addition, the influence of network formation on the solubility and swelling properties of the copolymers is examined.

EXPERIMENTAL

Polymer Preparation

Comonomer solutions containing various molar ratios of AA and ALA (both obtained from Polysciences, Inc., Warrington, PA) were bulk polymerized in the presence of 0.47 wt % benzoyl peroxide at 60°C in a constant temperature bath (±0.05°C) for 24 hr. In order to ensure complete conversion of unreacted monomer the resulting solid transparent ingots were subjected to the following serial heat treatment: ten days at 75°C (air), five days at 100°C (vacuum), and at least eight days at 120°C (vacuum). Specimens for the isothermal modulus tests were then machined to the required dimensions. All test samples were reheated at 120°C (vacuum) until constant weight was obtained (three to six weeks) whereupon the specimens were cooled and stored in a vacuum desiccator until needed.

Dynamic Mechanical Analysis

All dynamic mechanical properties were measured on a du Pont 981 dynamic mechanical analyzer (DMA). The operation of this instrument has been reviewed elsewhere,[19,20] and the same general experimental procedures were followed. In the present case, right circular cylindrical samples with nominal dimensions $L' \times r = 38.1 \times 1.5$ mm were gripped with an effective working length $L = 19.1$ mm, and the observed frequencies were converted into modulus values (Pa) by use of

$$\text{modulus} = \frac{2L^3(4\pi f^2 J - K_p/\pi)}{3r^4(2D + L)^2} \tag{1}$$

where f is the system frequency (Hz), J is the moment of inertia of sample arm (1.61×10^{-3} kg m²), K_p is the torsional spring constant of flexure pivot (0.38 N m rad⁻¹), D is the clamping distance (9.93×10^{-3} m), r is the sample radius (m), and L is the sample working length (m). The damping signal was converted into $\tan \delta$ values using

$$\tan \delta = VC/f^2 \tag{2}$$

where $\tan \delta$ is the ratio of energy dissipated to maximum potential energy stored per cycle, V is the system damping (mV), and C is the system constant (0.26 Hz²mV⁻¹ for an oscillation amplitude of 0.2 mm).

After setting the oscillation amplitude and the A/Z gain at 0.20 mm and 0.35, respectively, all scans were made at a heating rate of 10°C/min under N₂ gas over the temperature range from −100 to ~230°C. To account for temperature program and sample lag effects, a dynamic calibration procedure was followed.[19] By combining the temperature compensation with the continuous frequency and damping output, the modulus and $\tan \delta$ versus temperature plots were computed (Wang 2200 PCS-II) at discrete intervals.

Isothermal Modulus Studies

All tests were conducted in compression using an Instron universal testing machine at a crosshead velocity of 0.05 cm/min. The specimens, right circular cylinders of nominal dimensions 7.0 mm diameter × 14.0 mm length, were tested at 25°C in two stages: First the samples were preloaded to ~40 kg, held for 5 min and then released, thereby ensuring the removal of any major surface irregularities. Thereafter the specimens were reloaded to a maximum of 400 kg, and the sample deformation was measured at 0.0005-in. intervals by means of a Starrett dial indicator attached to the upper platen. Young's modulus E (Pa) was calculated from the initial straight line portion of the load–deformation curve according to

$$E = KPl/\Delta lA \tag{3}$$

where P is the load (kg), A is the area (cm^2), Δl is the deformation (cm), l is the initial sample length (cm), and K is the conversion factor, 9.8×10^4 (Pa cm^2/kg). The absence of significant geometric or machine deflection errors was confirmed by an external calibration using poly(methyl methacrylate) cylinders which yielded moduli of $(3.35 \pm 0.03) \times 10^9$ Pa for five measurements.

Sol–Gel Analysis

Sol-gel specimens (~100 mg in weight and of nominal dimensions 7.5 mm diameter × 2.5 mm length) were placed in Whatman extraction thimbles and carefully weighed (±0.1 mg). Each thimble containing one specimen was positioned in a Soxhlet extraction apparatus whereupon testing was conducted under a N$_2$ gas atmosphere using distilled water or acetone as the solvent. Extractions were continued until constant weight was obtained (about one week). The thimbles, containing the insoluble fraction, were then removed, slowly dried and reweighed. The sol fraction was then calculated from

$$\% \text{ sol} = 100(W_i - W_f)/W_i \tag{4}$$

where W_i is the initial weight (mg) and W_f is the final weight (mg). Sol fraction measurements were also made on the swelling specimens detailed below.

Swelling Characterization

Specimens, similar to those utilized in the sol-gel analysis, were placed in jars (one specimen per jar) containing about 250 ml of distilled water at approximately 25°C. The water in each jar was changed at daily intervals. Upon reaching the equilibrium level of swelling (about two weeks), the specimens were removed from the jars, weighed and dimensioned. The samples were then slowly dried, and the final weight and dimensions were measured. The swelling ratio q was then calculated according to

$$q_v = \frac{\text{volume of swollen gel}}{\text{volume of reconstituted unswollen gel}} \tag{5}$$

$$q_w = \frac{\text{weight of swollen gel}}{\text{weight of reconstituted unswollen gel}} \tag{6}$$

RESULTS AND DISCUSSION

In general the effects of crosslinking on the dynamic mechanical properties are most apparent at temperatures above the glass transition (T_g) as shown in Figure 1. Here the temperature dependence of the modulus and tan δ is shown for compositions for which the mole fraction of ALA (X) equals 0, 0.13, 0.28, and 0.57, respectively. Through the temperature range of glassy behavior, i.e., -100 to $\sim 100°$C, the moduli decrease very gradually to 25°C values of (4–6) $\times$ 10^9 Pa. By comparison shear modulus (G') values of (2 and 3) $\times$ 10^9 Pa have been reported for PAA[16] and a 94/6 AA–2 ethylhexyl acrylate copolymer,[17] respectively, while Pegoraro et al.[14] obtained an elastic modulus (E') of 9 $\times$ 10^9 Pa for PAA. Data for poly(methyl methacrylate) (PMMA) obtained via DMA measurements have previously been shown to be intermediate between shear and elastic values.[19] Hence, with the additional consideration that the present geometry ($L/2r \approx 6$) lies within the mixed mode deformation region, the present DMA results have been characterized as "modulus" rather than G or E.

As increasing amounts of ALA are added to the copolymer, the transition region is shifted to higher temperatures, and the magnitude of the modulus change at T_g is significantly decreased. A more detailed examination of this high-temperature region for all compositions tested (cf. Fig. 2) revealed a plateau in the rubbery zone for $X > 0.2$. The complete range of viscoelastic behavior for lightly crosslinked materials could not be determined because the modulus values were below the resolution limit of $\sim 10^7$ Pa. However, Tobolsky et al.[21] demonstrated the occurrence of rubbery plateaus ($E \cong 4 \times 10^6$ Pa) in various vinyl polymers crosslinked with tetraethylene glycol dimethacrylate (TEGDM) at mole fractions as low as 0.01–0.02. It is expected that the AA–ALA copolymers would behave similarly.
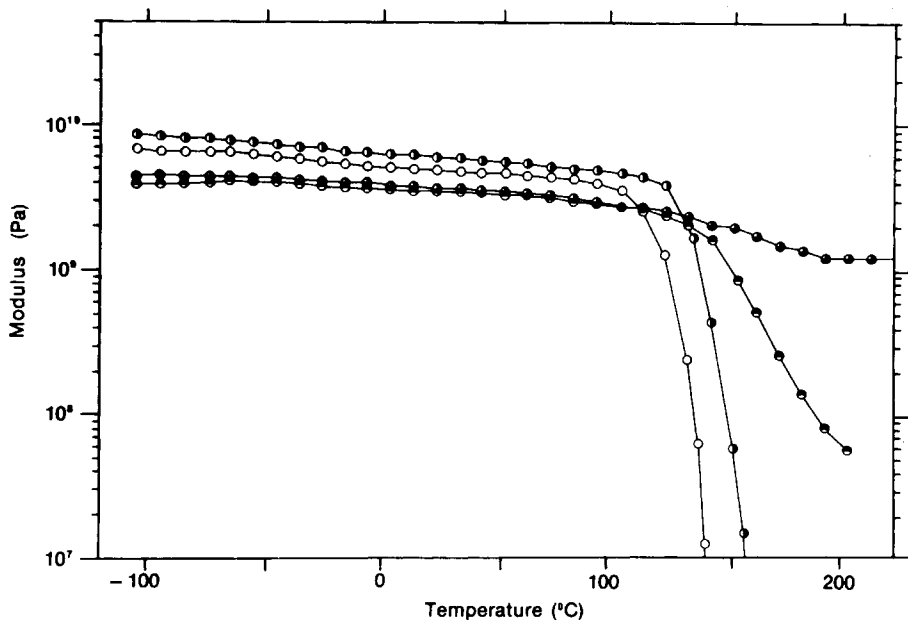

Fig. 1. Influence of initial concentration of ALA on the dynamic mechanical modulus of AA–ALA copolymers. ○, ◑, ◒, and ● correspond to X of 0, 0.13, 0.28, and 0.57, respectively.
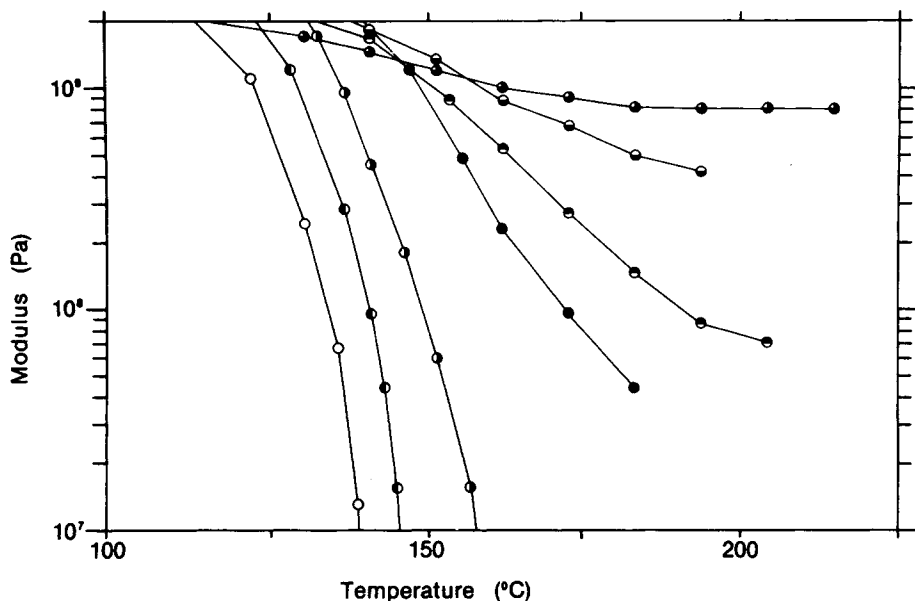
Fig. 2. Dependence of dynamic modulus on composition at temperatures above T_g for copolymers containing 0 (O), 0.06 (◑), 0.13 (◐), 0.20 (●), 0.28 (◒), 0.37 (◓), and 0.57 (◕) mole fraction ALA, respectively.

The most prominent feature of the tan δ versus temperature plots is the well-defined peak at 135°C for the PAA homopolymer (cf. Fig. 3). This peak, due to the glass transition decreases in magnitude, broadens and shifts to higher temperatures as X increases until at $X = 0.57$ ALA it can no longer be resolved. The temperature and magnitude of tan δ at T_g are summarized in Table I for each copolymer. Glass transition values for AA–ALA have been determined previously by differential scanning calorimetry (DSC).[22] These results, as well as those obtained from the dynamic mechanical analysis, are shown as a function of composition in Figure 4. Although there is no a priori reason why such a relationship should be linear, a regression analysis (cf. Table II) indicates that the dependence of T_g on X is highly significant. Whereas the slopes of the DMA
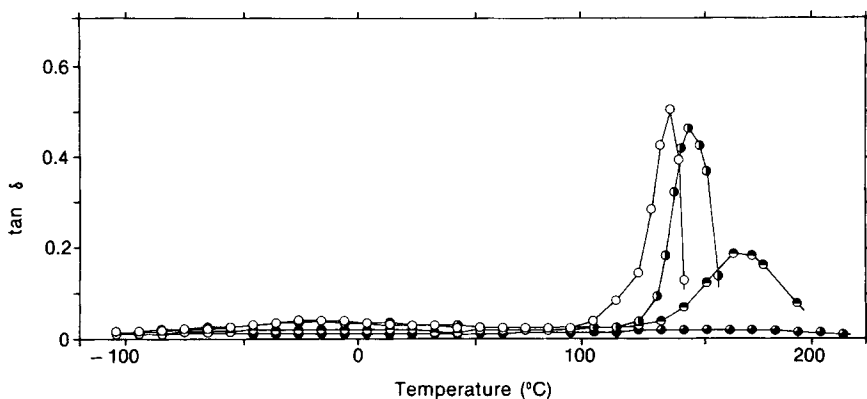

Fig. 3. Influence of composition (cf. Fig. 1) on the tan δ of AA–ALA copolymers.

TABLE I
Influence of Copolymer Composition on the Damping Behavior

Mole fraction of ALA, X	Measurement method		DSC
	Dynamic		
	T_g (°C)	$\|\tan \delta\|_{T=T_g}$	T_g (°C)[a]
0	135 ± 1.0 (2)[b]	0.55 ± 0.06 (2)	109
0.03	—[c]	—[c]	111
0.06	139 ± 3.0 (2)	0.52 ± 0.05 (2)	116
0.13	144 (1)	0.47 (1)	124
0.20	158 ± 3.0 (2)	0.30 ± 0.04 (2)	131
0.28	169 (1)	0.19 (1)	144
0.37	178 ± 4.2 (2)	0.06 ± 0.0 (2)	—[d]
0.57	—[d]	—[d]	—[d]

[a] See ref. 22.
[b] Sample size in parentheses.
[c] Not measured.
[d] None observed.

and DSC regression lines are virtually identical, the intercepts differ by approximately 23°C, indicating a T_g for the PAA homopolymer of 132 and 108°C, respectively. By comparison, values for the glass transition of PAA have been reported in the literature as 106–108°C.[23] However, it is recognized that a T_g measured by dynamic methods at 1 Hz tends to be about 15°C higher than that determined by thermal analysis techniques.[16] When an additional frequency shift factor of 5–7°C is taken into account because measurements were made at ~10 Hz,[24] there is good agreement between the two techniques.

Dynamic measurements have suggested that in the glassy region the modulus is a function of the copolymer composition (cf. Fig. 1). To better describe this relationship, E values were determined at room temperature (25°C) in compression at strain rates of 3.5×10^{-2} min^{-1} (cf. Table III). The results, shown in Figure 5, can be represented by similar linear regression lines (cf. Table IV). The intercept of the Instron regression line with the compositional extreme
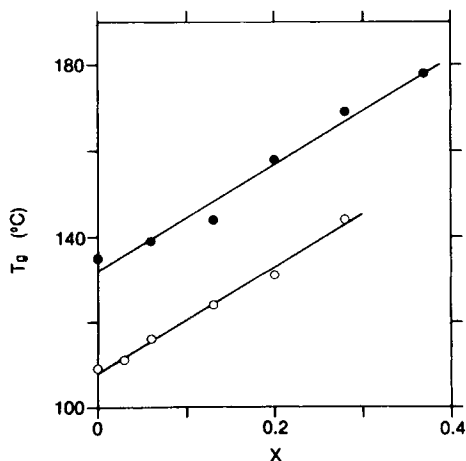

Fig. 4. Comparison of present T_g values (●) with those previously obtained from DSC measurements (○) (cf. ref. 22).

TABLE II
Statistical Analysis of Glass Transition Results

Measure-ment method	Linear regression equation	Number of data points	F	Level of signif-icance
Dynamic	T_g (°C) = 124.1X + 132.3	6	183	0.001
DSC	T_g (°C) = 123.5X + 108.1	6	529	0.001

delineate modulus values of (7.1 and 3.8) $\times 10^9$ Pa for PAA and ALA homopolymers, respectively. The difference in modulus between PAA and the extensively crosslinked ALA is attributed to the fact that in the glassy state the modulus is determined primarily by the strength of the secondary intermolecular forces.[24] This is demonstrated in a series of acrylate polymers: butyl acrylate,[25] methyl acrylate,[25,26] acrylic acid,[14-16] and zinc acrylate[15] for which modulus values of 1.3, 2.7–3.8, (4.2–8.8) $\times 10^9$, and 2 $\times 10^{10}$ Pa, respectively, have been determined. At the other extreme, values for crosslinked ALA could not be located in the literature. However, the obtained modulus for ALA compares favorably with a value of ~3.0 $\times 10^9$ Pa reported for the more commonly used EGDMA.[27] Although there is scatter among the data, particularly at low values of X, the results can be adequately described by a simple law of mixtures type relationship

$$E = E_1 (1 - X) + E_2 X \qquad (7)$$

where the subscripts 1 and 2 refer to the acrylic polymer and the crosslinking agent, respectively. This supports previous observations that the modulus is not greatly influenced by the presence of crosslinks below T_g.[26,28]

Heretofore the dynamic properties of the AA–ALA system have been described in terms of the initial concentration of tetrafunctional crosslinking agent. In order to characterize the network structure, solubility and swelling studies were conducted. Since a crosslinked polymer will swell in a liquid that normally is a solvent for the uncrosslinked state[28] the sol fraction (S) was determined for each copolymer composition using distilled water. The results (cf. Table V) indicate that even at the lowest concentration of ALA ($X = 0.03$), gelation is

TABLE III
Influence of Copolymer Composition on Modulus (25°C)

Mole fraction of ALA, X	Measurement method	
	Dynamic modulus $\times 10^{-9}$ (Pa)	Compression $E \times 10^{-9}$ (Pa)
0	4 6 ± 0.4 (2)[a]	6.4 ± 0.5 (4)
0.03	—[b]	7.1 ± 0.3 (3)
0.06	5.0 ± 0.4 (2)	7.4 ± 0.7 (4)
0.13	6.0 (1)	7.0 ± 0.5 (4)
0.20	4.6 ± 0.1 (2)	6.6 ± 0.4 (4)
0.28	3.5 (1)	5.9 ± 0.5 (4)
0.37	3.8 ± 0.3 (2)	5.7 ± 1.1 (2)
0.57	3.5 ± 0.3 (2)	5.5 ± 0.1 (3)
1.0	2.0 (1)	3.7 ± 0.2 (2)

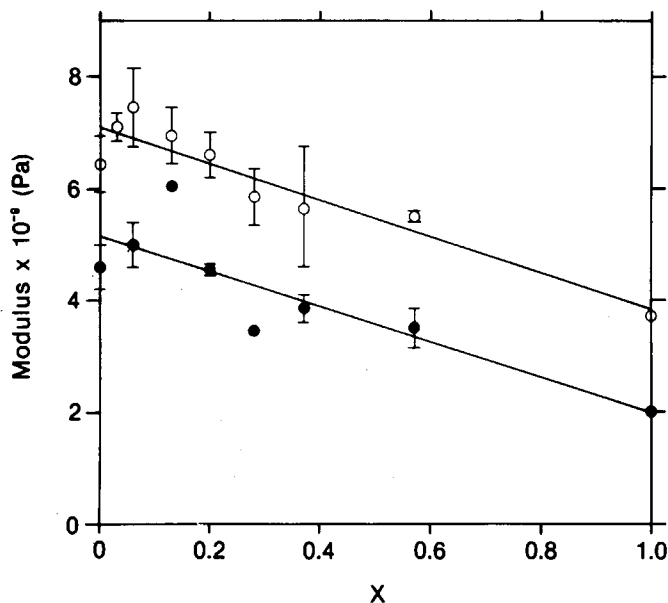[a] Sample size in parentheses.
[b] Not measured.

Fig. 5. Influence of composition on the 25°C modulus values as determined by dynamic (●) and compression (O) methods. The latter describe Young's modulus, while the former represent a mixed mode of deformation since $1 \leq L/2r \leq 10$.

practically complete, and further increases in X have little effect on S. Although monomer reactivity ratios have not been reported for the AA–ALA system, data for other AA–acrylic ester copolymers suggest that acrylic acid might be preferentially incorporated into the developing AA–ALA polymer.[23,29] Since such a structure would not favor early gelation, the observed solubility behavior is attributed to the crosslinking efficiency of the divinyl monomer which approaches a maximum value as $X \rightarrow 0$.[30–32] Indeed, previous studies of tetrafunctional allylic monomers polymerized by free radical methods have shown that even at low conversions the resulting crosslinked homopolymers contain little soluble polymer and the gel fraction is insoluble in a variety of solvents, including acetone, benzene, and dimethylformamide.[10,33]

Because of the intended biomedical applications of the material, there was particular interest in using water as the swelling medium. Consequently, swelling ratios were calculated by both volumetric (q_v) and gravimetric (q_w) methods. All specimens deformed isotropically, and the good agreement between q_v and q_w (cf. Table V) indicated that the samples did not contain appreciable numbers of internal defects.

Values of q_v are often used to obtain the average molecular weight between

TABLE IV
Statistical Analysis of 25°C Modulus Results

Measurement method	Linear regression equation	Number of data points	F	Level of significance
Dynamic	Modulus ($\times 10^{-9}$ Pa) = $-3.2X + 5.2$	8	16.9	0.01
Compression	E ($\times 10^{-9}$ Pa) = $-3.3X + 7.1$	9	60.2	0.001

TABLE V
Solubility and Swelling Parameters

Mole fraction of ALA, X	Swelling ratio, q_v	Swelling ratio, q_w	Soluble fraction, S ($\times 10^2$)	$M_c \times 10^{-3}$ [a]
0	∞	∞	99.3 ± 1.9 (6)	
0.03	2.9 ± 0.0 (2)[b]	2.9 ± 0.0 (2)	2.5 ± 4.0 (3)	3.0
0.06	2.1 ± 0.0 (5)	2.2 ± 0.1 (5)	3.4 ± 0.8 (4)	1.8
0.13	1.6 ± 0.0 (5)	1.9 ± 0.2 (4)	2.6 ± 0.8 (5)	1.1
0.20	1.4 ± 0.0 (6)	1.6 ± 0.1 (6)	2.2 ± 1.1 (7)	0.71
0.28	1.3 ± 0.0 (5)	1.4 ± 0.1 (5)	1.5 ± 1.5 (7)	0.51
0.37	1.2 ± 0.0 (3)	1.2 ± 0.1 (3)	−0.1 ± 0.7 (4)	0.40[c]
0.57	1.0 ± 0.0 (3)	1.1 ± 0.0 (3)	0.0 ± 0.2 (4)	
1.0	1.0 ± 0.0 (2)	1.0 ± 0.1 (2)	0.1 ± 0.3 (3)	

[a] See ref. 22.
[b] Sample size in parentheses.
[c] Extrapolation of Fig. 2, ref. 22.

crosslinks M_c by means of the well known Flory equation.[34] However, because of the inherently inhomogeneous nature of certain network structures, some caution must be exercised in the use of this parameter for materials crosslinked by means of free radical copolymerization.[35-37] Although values of M_c become increasingly less accurate as the crosslink density increases, the Flory equation has been used to qualitatively describe a number of network polymers.[38-41] Application of this relationship to the present data, however, did not yield satisfactory results.

The molecular weight between crosslinks may also be obtained by other methods. For example, values of M_c have previously been calculated for a number of copolymers[12,42,43] from Nielsen's semiempirical relationship[28]

$$M_c = (3.9 \times 10^4)/(T_g - T_{g0}) \qquad (8)$$

where T_g (°C) is the glass transition temperature of the crosslinked polymer and T_{g0} (°C) is the glass transition temperature of an uncrosslinked polymer having the same chemical composition as the crosslinked polymer. Application of this equation to the AA–ALA system (cf. Table V) indicated that M_c decreases from 3000 to 510 over the composition range $X = 0.03$–0.28.[22] By making use of the T_g value of 178°C for $X = 0.37$ obtained from dynamic measurements (cf. Fig. 4 and Table I), an M_c of 400 may be predicted by means of eq. (8) and the data from ref. 22.

The swelling behavior of the AA–ALA copolymers is shown in Figure 6 where q_v is plotted as a function of M_c. In addition, swelling data are presented for highly crosslinked allyl methacrylate (AMA),[38] purified natural rubber reacted with dicumyl peroxide,[39] amine-cured epoxy resin,[40] and radiation crosslinked poly(vinyl alcohol) (PVA) hydrogels.[41] In all these cases, results were obtained over the entire range of M_c using the Flory equation, although the authors generally acknowledged the increasingly qualitative nature of their estimates as M_c decreased, particularly below $M_c \simeq 2 \times 10^3$. Although Bell's work and the present effort represent two independent determinations in that highly crosslinked region, the observed linear dependence may be fortuitous, since Bell computed his M_c values from an assumed reaction stoichiometry and we eval-
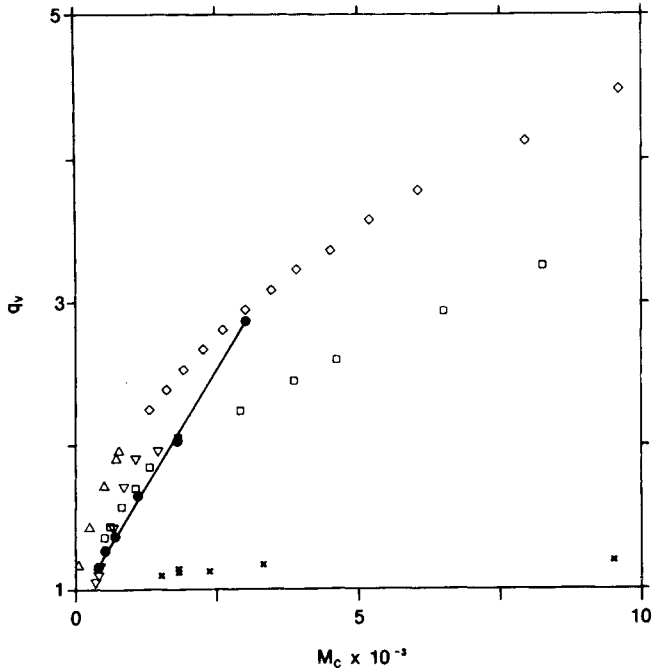
Fig. 6. Dependence of the swelling ratio on the degree of crosslinking for AA-ALA (●), AMA (◊) (cf. ref. 38), pure natural rubber (□) (cf. ref. 39), epoxy (△ and ▽) (cf. ref. 40), and PVA (x) (cf. ref. 41).

uated M_c by means of Nielsen's expression.   Whether such behavior indicates a real similarity in the response of the respective highly crosslinked materials warrants further study.

References

1. A. R. Greenberg, I. L. Kamel, S. Dubin, and A. Miller, *J. Biomed. Mater. Res.*, 12, 929 (1978).
2. A. Franck, *Chem. Ztg. Chem. Appar.*, 91, 7 (1967).
3. M. C. McGaugh and S. Kottle, *J. Polym. Sci., Part B*, 5, 817 (1967).
4. A. Eisenberg, T. Yokoyama, and E. Sambalido, *J. Polym. Sci., Part A-1*, 7, 1717 (1969).
5. S. Combet and J. Lleras, *C.R. Acad. Sci. Ser. C*, 270, 1280 (1970).
6. A. R. Greenberg and I. L. Kamel, *J. Polym. Sci.*, 15, 2137 (1977).
7. B. D. Ratner and A. S. Hoffman, "Synthetic Hydrogels for Biomedical Applications," in *Hydrogels for Medical and Related Applications*, J. D. Andrade, Ed., American Chemical Society, Washington, D.C., 1976.
8. C. E. Schildknecht, *Allyl Compounds and Their Polymers*, Wiley-Interscience, New York, 1973, chap. 25.
9. M. Donati and M. Farina, *Makromol. Chem.*, 60, 233 (1963).
10. G. F. D'Alelio and T. R. Hoffend, *J. Polym. Sci., Part A-1*, 5, 323 (1967).
11. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, chap. 7.
12. T. Murayama and J. P. Bell, *J. Polym. Sci., Part A-2*, 8, 437 (1970).
13. A. V. Tobolsky, D. Katz, R. Thach, and R. Schaffhauser, *J. Polym. Sci.*, 62, S176 (1962).
14. M. Pegoraro, L. Szilagyi, A. Penati, and G. Alessandrini, *Eur. Polym. J.*, 7, 1709 (1971).
15. J. E. Fields and L. E. Nielsen, *J. Appl. Polym. Sci.*, 12, 1041 (1968).

16. J. Kolarik, *J. Macromol. Sci. Phys.*, **15**, 371 (1978).

17. W. E. Fitzgerald and L. E. Nielsen, *Proc. R. Soc. London Ser. A*, **282**, 137 (1964).

18. T. Mori, K. Imada, R. Tanaka, and T. Tanaka, *Polym. J.*, **10**, 45 (1978).

19. R. P. Kusy and A. R. Greenberg, *J. Therm. Anal.*, **18**, 117 (1980).

20. R. P. Kusy and A. R. Greenberg, *Thermochim. Acta*, **37**, 53 (1980).

21. A. V. Tobolsky, D. Katz, M. Takahashi, and R. Schaffhauser, *J. Polym. Sci., Part A*, **2**, 2749 (1964).

22. A. R. Greenberg and R. P. Kusy, *J. Appl. Polym. Sci.*, **25**, 1785 (1980).

23. *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, Chaps. 2 and 3.

24. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Vol 1, Marcel Dekker, New York, 1974, Chap. 4.

25. A. V. Tobolsky and M. Takahashi, *J. Appl. Polym. Sci.*, **7**, 1341 (1963).

26. J. Heijboer, "Mechanical Properties and Molecular Structure of Organic Polymers," in *Physics of Non-Crystalline Solids*, J. A. Prins, Ed., North-Holland, Amsterdam, 1965.

27. A. V. Tobolsky, "Viscoelastic Properties of Polymers." in *Polymer Science and Materials*, A V. Tobolsky and H. F. Mark, Eds., Wiley-Interscience, New York, 1971.

28. L. E. Nielsen, *J. Macromol. Sci. Rev. Macromol. Chem.*, **3**(1), 69 (1969).

29. D. C. Allport, "Free Radical Polymerization of Vinyl Monomers," in *Block Copolymers*, D. C. Allport and W. H. Janes, Eds., Halsted, New York, 1973.

30. S. Loshaek and T. G. Fox, *J. Am. Chem. Soc.*, **75**, 3544 (1953).

31. J. Hasa and J. Janacek, *J. Polym. Sci., Part C*, **16**, 317 (1967).

32. Y. Diamant, S. Welner, and D. Katz, *Polymer*, **11**, 498 (1970).

33. H. Kamogawa, S. Furuya, and M. Kato, *J. Polym. Sci., Part C*, **23**, 655 (1968).

34. P. J. Flory, *Principles of Polymer Chemistry*, Cornell U. P., Ithaca, N.Y., 1953, chap. 13.

35. K. Dusek, "Inhomogeneities Induced by Crosslinking in the Course of Crosslinking Copolymerization," in *Polymer Networks: Structure and Mechanical Properties*, A. J. Chompff and S. Newman, Eds , Plenum, New York, 1971.

36. F. Rietsch, D. Daveloose, and D. Froelich, *Polymer*, **17**, 859 (1976).

37. J. P. Munch, S. Candau, and G. Hild, *J. Polym. Sci., Part B*, **15**, 11 (1977).

38. G. M. Bristow, *Trans. Faraday Soc.*, **54**, 1239 (1958).

39. P. Mason, *Polymer*, **5**, 625 (1964).

40. J. P. Bell, *J. Polym. Sci., Part A-2*, **6**, 417 (1970).

41. N. A. Peppas and E W. Merrill, *J. Appl. Polym. Sci.*, **21**, 1763 (1977).

42. E. P. Otocka and F. R. Eirich, *J. Polym. Sci., Part A-2*, **6**, 895 (1968).

43. M. Pineri, C. Meyer and A. Bourret, *J. Polym. Sci., Part B*, **13**, 1881 (1975).