Influence of Crosslinking on the Glass Transition of Poly(acrylic Acid)

INTRODUCTION

Many of the physical and mechanical properties of a polymer are greatly influenced by the presence of crosslinks. The effectiveness of such a network is manifested by the change in the glass transition temperature T_g, which occurs as the crosslink density is increased.[1-3] It is generally acknowledged that this T_g shift is made up of a copolymer ($\Delta_{cop}T_g$) as well as a crosslinking component ($\Delta_{x1}T_g$).[4,5] Whereas the latter always increases T_g, the former may either increase or decrease T_g depending on the chemical nature of the added comonomer.[6,7] If the magnitude of the copolymer effect can be determined, then the network polymer can be approximately described by estimating the number-average molecular weight between crosslinks M_c determined from the empirical relationship of Nielsen[8]

$$M_c = (3.9 \times 10^4)/\Delta_{x1}T_g \qquad (1)$$

where $\Delta_{x1}T_g = T_g - T_{g0}$, T_g is the glass transition temperature (°C) of the crosslinked copolymer, and T_{g0} is the glass transition temperature (°C) of an uncrosslinked copolymer having the same chemical composition as the crosslinked polymer. This relationship has been used to describe a number of crosslinked polymers.[9-11]

In the present case highly crosslinked poly(acrylic acid) (PAA) was prepared by the copolymerization of AA monomer with increasing amounts of a tetrafunctional monomer, allyl acrylate (ALA), and the T_g's of the resulting polymers were determined by differential scanning calorimetry (DSC). Similarly, identical compositions of AA–n-propyl acrylate (nPA) copolymers were prepared and tested. Since, except for the presence of crosslinks, AA–nPA and AA–ALA copolymers have similar chemical structures, M_c could be calculated for each composition by means of eq. (1).

EXPERIMENTAL

The AA–ALA and AA–nPA copolymers (cf. Table I) were prepared by the free radical polymerization (0.47 w/o benzoyl peroxide) of the respective monomers (Polysciences, Inc., Warrington, PA) at 60°C for 24 hr. Postpolymerization heat treatments at 80 and 120°C under vacuum for 10 days for the AA–nPA and AA–ALA copolymers, respectively, were carried out to ensure complete conversion. All samples were subsequently stored in a vacuum desiccator to prevent sorption of water vapor.

DSC scans were made on powdered 10.00 ± 0.10-mg samples in covered aluminum pans using a du Pont 990 thermal analyzer at a heating rate of 10°C/min under N_2.

In order to eliminate any effects of prior thermal history, each sample was first heated 40°C above the transition region, held for 5 min, and then quenched. The initial scan was then made, the sample again quenched from above T_g, and a second run conducted. The glass transitions of these subsequent scans were all within ± 2°C of the initial value. The reported T_g values represent the average of these two runs. Two additional samples (~10 mg) were also tested for several AA–ALA compositions. Although not included in the analysis, these data are denoted by parentheses in Table I.

RESULTS AND DISCUSSION

The thermal behavior of PAA homopolymer is shown in the topmost scan of Figure 1 where the glass transition is defined by the intersection of tangent lines drawn through the baseline and the descending portion of the trace. The obtained value of 109°C compares favorably with previously published results of 106°C.[12] Additions of ALA result in an increase in T_g accompanied by shallower, less distinct transition regions until T_g could no longer be resolved (cf. Fig. 1, scans b–d). In contrast the glass transitions of the AA–nPA copolymers were all well defined. But unlike the ALA, the nPA additions monotonically decreased T_g until a minimum value of −38°C was measured for the nPA

TABLE I
Summary of Experimental Results

X	T_{g0} (°C)	T_g (°C)	$\Delta_{x1}T_g$ (°C)	$M_c \times 10^{-3}$	n_c
0	109	109 (109,110)	0	—	—
0.03	98	111	13	3.0	82
0.06	94	116 (115,116)	22	1.8	48
0.12	89	124 (122,121)	35	1.1	29
0.20	76	131 (126,129)	55	0.71	18
0.28	67	144 (144,147)	77	0.51	12
0.36	56	—[a]	—	—	—
1.00	−38	—	—	—	—

[a] None observed.

homopolymer (cf. $T_g = -37$°C, ref. 12). These results are illustrated in Figure 2 (top), where T_g is plotted for each copolymer as a function of mole fraction of the respective ester addition. From these values the compositional dependence of $\Delta_{x1}T_g$ was obtained (Fig. 2, bottom), and the M_c calculated via eq. (1) (cf. Table I).

The degree of crosslinking may also be represented by the number of backbone atoms between adjacent crosslinks n_c, which for vinyl monomers can be obtained from[7]

$$n_c = 2M_c/M_e \tag{2}$$

where M_e is the effective average molecular weight of a repeat unit. Assuming a random copolymer structure and a dependence of M on the initial molar ratio between the monomers

$$M_e = M_{x1}X + M(1 - X) \tag{3}$$

where X, M_{x1}, and M are the mole fraction of crosslinking agent, and the molecular weights of the crosslinking agent and the vinyl monomer, respectively. The obtained values of n_c are summarized in Table I.
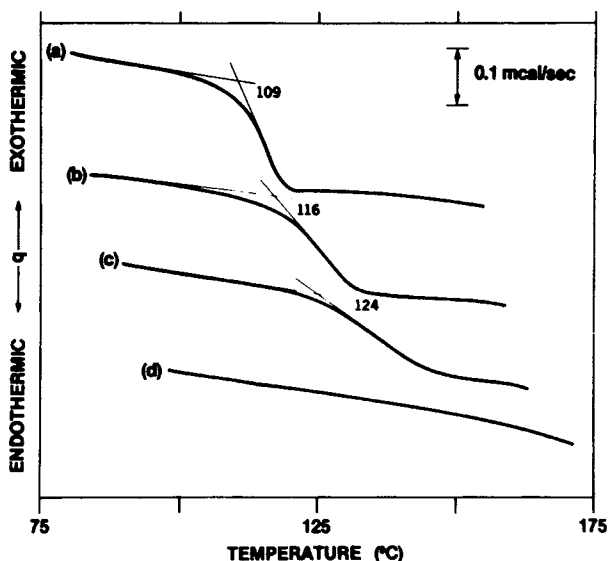

Fig. 1. Glass transition of AA–ALA copolymers containing (a) 0, (b) 0.06, (c) 0.12, and (d) 0.36 mole fraction ALA, respectively.
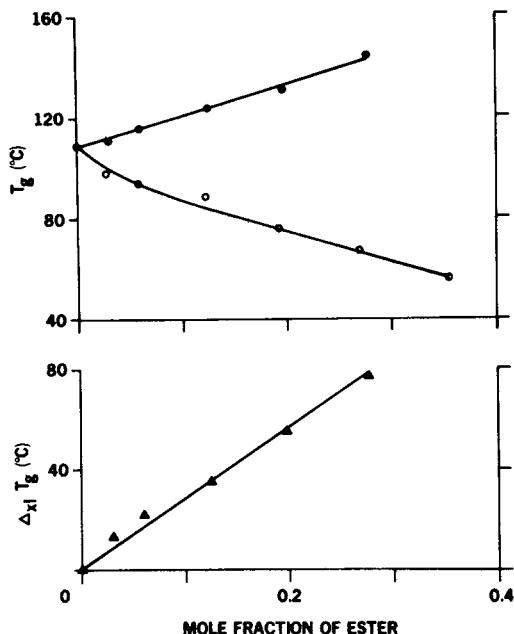
Fig. 2. Influence of composition on the glass transitions of AA–ALA (●) and AA–nPA (○) copolymers, and the net crosslinking effect, $\Delta_{x1}T_g$ (▲).

In analogous fashion these methods were used to analyze the glass transition data obtained by Loshaek[4] for methyl methacrylate (MMA) crosslinked with ethylene glycol dimethacrylate (EGDMA) and structurally similar copolymers of MMA-ethylene glycol monomethacrylate/monoisobutyrate. In addition, although determined by stoichiometric methods, Diamant et al.[13] reported n_c as a function of composition for isobutyl methacrylate (IBMA) crosslinked by EGDMA. Values for the two EGDMA crosslinked polymers are compared to those for the AA–ALA material in Figure 3 where a geometric regression line has been drawn through the data. The results are in good agreement and indicate a highly significant dependence of crosslink density on composition ($p < 0.01$). However, although these limited data can be satisfactorily described by a single curve, the general applicability of such a relationship requires further study.
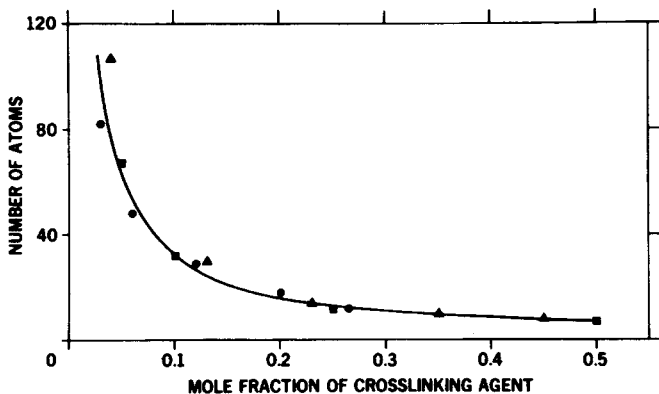

Fig. 3. Relationship between the number of atoms between crosslinks in AA–ALA (●) (present work), MMA–EDGMA (▲) (ref. 4), and IBMA–EGDMA (■) (ref. 13) copolymers and the initial concentration of crosslinking agent.

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A. R. GREENBERG
R. P. KUSY

Dental Research Center
University of North Carolina
Chapel Hill, North Carolina 27514