The Viscosity K for Poly-(Glycidyl Methacrylate)

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LETTER TO THE EDITOR

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Poly-(Glycidyl Methacrylate)

Poly-(glycidyl methacrylate),

$$
\begin{array}{c}
CH_3 \\
| \\
-\!\!\left[CH_2\text{-}C\;-\!\right]_{\overline{n}} \\
| \\
COOCH_2\,CHCH_2 \\
\backslash \;\; / \\
O
\end{array}
$$
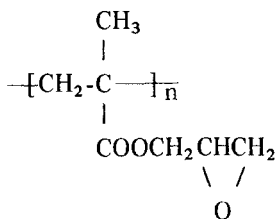
(I)

is an interesting polymer which can undergo many useful postreactions. We have used it to prepare chelating polymers by reacting it with iminoacetic acid and other amino-containing ligands. Though (I) had been prepared previously [1], it had been characterized only in terms of inherent or intrinsic viscosity. Since, for our purposes, it was important to establish the molecular weights of the polymers used in our study, we established M_n by osmometry and correlated these values to the viscosity relationship.

$$[\eta] = K_V M^a \tag{1}$$

Polymerizations of glycidyl methacrylate,

$$
\begin{array}{c}
CH_3 \\
| \\
CH_2\!=\!C\text{---}COOCH_2\,CHCH_2 \\
\backslash \;\; / \\
O
\end{array}
$$
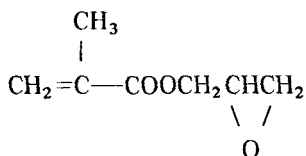
(II)

in heptane or benzene, initiated by benzoyl peroxide, consistently yielded large amounts of insoluble cross-linked polymers. Linear, soluble polymers of (I) were readily prepared by the free radical polymerization of (II) in 2-butenone using 2,2′-azobisisobutyronitrile or benzoyl peroxide as initiators. The following are typical polymerizations:

A. Benzoyl peroxide (0.25 g) was dissolved in freshly distilled glycidyl methacrylate (25.00 g) maintained under nitrogen, and the solution was added to 125 ml of freshly distilled 2-butanone. The resulting solution was contained in a 250-ml, three-necked flask which was covered with aluminum foil and equipped with a water condenser, thermometer, nitrogen inlet and outlet, heating mantle, and magnetic stirrer. The reaction mixture was stirred and slowly heated to 79°C in a nitrogen atmosphere. Five-milliliter aliquots were removed from the reaction mixture at various times, and the polymer was precipitated and washed with 2-propanol. The per cent conversions to polymer at 30, 75, 120, 195, and 270 min were 0.1, 24.1, 35.2, 66.9, and 87.8%, respectively. After 4.5 hr at 79°C, the turbid reaction mixture was cooled to room temperature and filtered; the polymer was precipitated from the clear filtrate using 2-propanol. The white product was washed four times with approximately 30-ml portions of 2-propanol and dried in vacuo at room temperature for 48 hr; the yield of polymer (I) was 21.03 g (84.1% yield). The infrared spectrum of (I) was identical to that previously reported [1]. The C=C vinyl absorption that occurs at 1643 cm^{-1} in the spectrum of the monomer was absent from the polymer spectrum. The intensity of the peak at 3000 cm^{-1}, which has been assigned to the CH stretching vibration of the epoxy ring [3], and the intensities of the peaks at 1250, 900, and 840 cm^{-1}, which have been assigned to the epoxy ring vibrations [2, 3], were equal to the intensities found for the same peaks in the monomer spectrum. This strongly indicates that the epoxy rings were not affected by the polymerization reaction. The ester peak at 1725 cm^{-1} was the strongest peak in the polymer spectrum.

The polymer was also analyzed for epoxy oxygen by the method of King [4]. It was found to contain 10.70% epoxy oxygen as compared with the 11.2% that was found in monomeric glycidyl methacrylate. This analysis was in close agreement with the 10.77% epoxy oxygen that was found in the poly(glycidyl methacrylate) made by Ravve and Khamis [1]. The dried polymer (I) was soluble in 2-butanone, dioxane, acetone, and N,N-dimethylacetamide. It was insoluble in water, methanol, 2-propanol, and hexane.

Anal: Calculated for $-(C_7H_{10}O_3)_n$: C, 59.15; H, 7.04; O, 33.80. Found: C, 59.10; H, 7.13; O, 33.77.

B. Dodecanethiol (0.125 g, 0.5% by weight on the monomer) was added to the system described in A above, and the reaction was performed at 79°C for 5 hr. The polymer was precipitated, isolated, washed, and dried as described above. The yield of polymer (II) was 20.0 g (80% yield of white product, epoxy oxygen 10.6%).

Anal: Calculated for $-(C_7H_{10}O_3)_n-$: C, 59.15; H, 7.04. Found: C, 58.61; H, 7.06; S, 0.82.

The sulfur content of (II) corresponds to a molecular weight of 7830.

Polymer (I) was separated into five major fractions by dissolving it in 2-butanone, filtering the solution and slowly adding 2-propanol with rapid stirring to the solution, and isolating the precipitated products by centrifugation. The five fractions were refractionated twice, and four final fractions, (Ia), (Ib), (Ic), and (Id), were selected for measurements. The intrinsic viscosities of the polymers were determined in 2-butanone using a semimicro Cannon-Ubbelohde dilution viscometer. Both the solvent and the solutions were filtered prior to their use. The temperature was maintained at 20 ± 0.02°C. The reduced viscosities were calculated from the efflux times measured at at least three solution concentrations. The intrinsic viscosities were calculated by extrapolation of the reduced viscosities to zero concentration.

The number average molecular weights of (Ia) and (Ic) were determined by vapor phase osmometry. The measurements were performed on a Mechrolab Model 302 vapor pressure osmometer equipped with a 37°C thermostat and a nonaqueous probe. Freshly distilled reagent grade 2-butanone was used as the solvent. A calibration factor characteristic of the instrument-thermostat-probe solvent combination was obtained using recrystallized benzil (molecular weight 210.2) as a standard solute. The molecular weight, M_n, was calculated from the equation

$$\frac{\Delta R}{C} = \frac{K}{M} + AC \tag{2}$$

by extrapolating a plot of $\Delta R/C$ vs C to zero concentration and then dividing the calibration factor (K) by the resulting intercept. In this equation, ΔR is the dekastat resistance reading for a given concentration, C, and A is the concentration coefficient.

The following measured intrinsic viscosities of the fractionated polymers and M_n were related to M in Eq. (1) in the form of

$$[\eta] = KM_n^a \tag{3}$$

Polymer	Weight, g	$[\eta]$	M_n
(I)	21.03	0.242	—
(Ia)	1.06	0.380	44,980
(Ib)	1.43	0.170	16,460
(Ic)	1.27	0.114	9,988
(Id)	0.98	0.082	6,619
(II)	20.00	0.092	—

The value of exponent a in Eq. (1) has been found [5] to be 0.8 for the majority of the acrylate and methacrylate polymers. Using this value, the calculated value of K from Eq. (3) is 7.2 × 10⁻⁵ and Eq. (1) can be written as

$$[\eta] = 7.2 \times 10^{-5} \, M^{0.8} \qquad (4)$$

This value is consistent with the K values found [5] for the closely related polymers: 7.1×10^{-5} for poly(methyl methacrylate); 9.7×10^{-5} for poly(n-butyl methacrylate); 7.0×10^{-5} for poly(cyclohexyl methacrylate: and 7.15×10^{-5} for poly(n-butyl acrylate).

The average molecular weights of the unfractionated polymers calculated from Eq. (4) and measured by osmometry reflect the heterogeneity of the products:

Polymer	Calculated $\bar{M}_\eta$	Found $\bar{M}_n$
(I)	25,590	24,170
(II)	7,640	7,510

During the course of this work, lower-molecular-weight polymers similar to (II) were prepared using dodecanethiol as the chain transfer [6] agent at concentrations varying from 0.1 to 0.5% by weight on the monomer, and the transfer constant, C_t, calculated [7] using Eq. (5) and C_t, was found to be 0.02.

$$\frac{1}{\bar{M}_n} = \frac{1}{\bar{M}_{n,o}} + C_t \frac{(t)}{(m)} \qquad (5)$$

where $\bar{M}_n$ = number average molecular weight obtained in the presence of transfer agent t

$\bar{M}_{n,o}$ = number average molecular weight obtained in the absence of transfer agent t

C_t = transfer constant

(t) = transfer agent concentration

(m) = monomer concentration

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