NOTES

Determination of Glass Transition Temperatures of Cholesteryl Methacrylate–Methyl Methacrylate Copolymers by Gas Chromatography

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Since Lavoie and Guillet¹ measured the glass transition temperatures (T_g) of poly(vinyl chloride), polystyrene and poly(methyl methacrylate), the inverse gas chromatographic method (IGC) has been used for studying the physical properties of polymers. Using this method, studies on the small molecular liquid crystals have been reported by Matire *et al.*,² Willey *et al.*,³ and Shōji *et al.*,⁴ etc. However, this method has not yet been applied to thermotropic liquid crystalline polymers.

This study shows that the reproducible T_g of a copolymer can be determined by the IGC method from the retention diagram of decane for copolymers.

A differential scanning calorimetry (DSC) did not give correct T_g of cholesteryl methacrylate(ChMA)–methyl methacrylate(MMA) copolymers, because of poor reproducibility.

Materials

All the solvents employed were distilled prior to use. Cholesterol was used without further purification. The ChMA was prepared by reacting cholesterol with methacryloyl chloride in a solvent mixture of ether and toluene (1:1 by volume) at 80°C for 24 h. The reaction

mixture was then poured into methanol and the precipitated product was isolated with a yield of 63%. White needle-like crystals (mp 107.5°C) were obtained by three repeated precipitations.

The IR spectra of ChMA were measured with a Nippon Bunko 403-G spectrophotometer. ¹H NMR and ¹³C NMR spectra were obtained with a JEOL FT-100. The monomer was soluble in benzene, chloroform and ether but insoluble in methanol and acetone.

Solution Polymerization

The homopolymerization of ChMA and copolymerization of ChMA–MMA were carried out by the method of Blumstein *et al.*⁵ for comparison of T_g data. The polymerization was carried out in a benzene solution (total monomer concentration: 0.1 mol l⁻¹) at 60°C, using azobisisobutyronitrile (AIBN) as the initiator (0.01 mol l⁻¹) for 24 h. The copolymers were precipitated from the benzene solution into methanol and the remaining monomer in the product was completely removed by ether extraction. The products were dried at room temperature under vacuum.

The composition of the copolymers was

determined from the ^1H NMR spectra. All the copolymers were soluble in benzene, chloroform, carbon tetrachloride, and THF but insoluble in methanol and ether.

Molecular Weight

Measurements of the number-average molecular weight (M_n) of the copolymers were made by gel-permeation chromatography with the apparatus of Waters Associates GPC-200, under the following conditions: solvents, tetrahydrofuran (THF); polymer concentration, 0.02 or 0.025%; temperature, 40 or 60°C; column, polystyrene gel ($8.5 \times 10^3 \text{ \AA}$); standard materials, polystyrenes. The M_n of copolymers are listed in Table I.

Inverse Gas Chromatography

The gas chromatographic experiments were carried out with a Yanaco, G-180 model, equipped with a thermal conductivity detector (recorder sensitivity; 1 mV). The column was a stainless steel tube 75 cm long and 4 mm in outer diameter. Helium was employed as the carrier gas whose flow rate was controlled to 60 ml min^{-1} , using a precision auto bubble

flow meter (Standard Technology, SF-11M model). The support was a Chromosorb-G AW DMCS (60–80 mesh). The copolymer was dissolved in benzene, and then the support was added. The column filler covered with a thin film of the copolymer, was prepared by slowly evaporating the solvent. The solvent was completely removed under vacuum. 20 wt% loading of copolymer was employed, on the basis of the results obtained for the low molecular liquid crystals.⁴ The amount of copolymer deposited on the support was determined by gravimetric measurement. The gas flow rate was 60 ml min^{-1} . Decane as the probe molecule without further purification was injected into the gas flow with a $0.1 \mu\text{l}$ capacity micro syringe from Precision Sampling Co.

The relative retention time of decane was estimated in comparison with that of air, and the relative retention volume (V_r) was calculated from the relative retention time and flow rate of carrier gas. It is known that V_r significantly depends on the amount of injected solute, but V_r should be constant according to Henry's law at infinite dilution. Since the peak height was proportional to the amount of injected solute, V_r at infinite dilution (V_r^0) was determined by extrapolating the peak height to zero. The extrapolation corresponded to that in the low concentration region of probe molecule proposed by Nakajima *et al.*¹² Moreover, V_r^0 was reduced to the specific retention volume (V_g^0), and V_g^0 defined by equation 1 was calculated.

$$V_g^0 = 273 V_r^0 / TW \quad (1)$$

where T is the column temperature (K) and W , the weight of coated polymer.

Retention Diagrams of Decane for the Copolymers

The partition of a solute molecule between the moving and stationary phases is expressed in terms of V_g^0 in gas chromatography, and is a characteristic parameter of the solute-solvent

Table I. Properties of ChMA-MMA copolymers

Mol. fraction of ChMA	Yield	M_n
	%	
0.92	83.5	80200
0.85	68.9	72800
0.72	90.4	45000

Table II. Column parameters for ChMA-MMA copolymers

Column No.	Content of ChMA	Column loading
	mol%	g
1	92	0.7562
2	85	0.7634
3	72	0.7057

system investigated. A plot of logarithmic V_g^0 versus the reciprocal absolute temperature, the so called retention diagram, must be straight unless a change occurs in the state of the stationary phase, such as that from solid to liquid. This is because the slope is closely related to the heat of solution.

Figure 1 shows the retention diagram of decane for the ChMA-MMA copolymer. The plots are linear, although they deflect just at temperatures corresponding to T_g .

In gas liquid chromatography in which bulk sorption is due only to the retention mechanism, V_g^0 should be independent of the mass of stationary phase. Similarly, in gas solid chromatography, the meaningful datum is the surface retention volume, that is, the retention volume per unit surface area of the absorbent. It has been shown that, when both effects are present, retention data for a low molecular weight stationary phase can be satisfactorily represented by the following relation.⁶

$$V_r = K_b W_1 + K_a A_1 \quad (2)$$

where V_r is the retention volume, K_b and K_a , the partition coefficients for the bulk sorption and surface adsorption, and W_1 and A_1 are the mass and surface area of stationary phase. If both retention mechanisms are operative in the stationary phase near T_g , eq 2 should account for the retention diagram of crystalline polymers.

In this experiment, the N -shaped retention diagram could not be observed, but the diagram showed two straight lines having different slopes shown in Figure 1; similar linear plots were obtained in the case of copolymers containing 72, 85 and 92 mol% of ChMA.

V_g^0 linearly decreased with increasing temperature until the temperature corresponding to T_g , and then V_g^0 plots decreased along with another linear line as shown in Figure 1. A point of discontinuity was obtained as an intersection of the two straight lines.

In the case of small molecular liquid crys-

Figure 1. Temperature dependence of specific retention volume (V_g^0) of decane for ChMA-MMA copolymers. ●, ChMA-MMA (0.72/0.28); ▲, ChMA-MMA (0.85/0.15); ○, ChMA-MMA (0.92/0.08).

Table III. Least squares analysis of the retention data

Column No.	ChMA %	Correlation coefficients		Intersection °C	$T_g^{5,11}$ °C
		at low temp	at high temp		
1	92	0.998	0.997	162	167
2	85	0.999	0.998	150	160
3	72	1.000	0.995	145	148

tals,²⁻⁴ the N -shaped retention diagram could not be observed but the transition occurred at the point of discontinuity in the straight line.

In Figure 1, the copolymer containing the more rich in ChMA tends to show more indistinct discontinuity, probably because the homopolymers of cholesteryl methacrylate⁷⁻⁹ are amorphous.

Since it is not necessarily confirmed that the discontinuity from the retention diagram corresponds to the T_g of copolymer, the discontinuities were compared with the T_g values estimated from the deformation test by Blumstein *et al.*^{5,11} in Table III.

Although a considerable difference is observed for the sample of 85 mol% ChMA, it may be assumed that both values are closely related to each other.

One of the authors reported that these copolymers began to show a mesomorphic state from the temperature of T_g .¹⁰ Even if the copolymers are amorphous, the thermodynamically stable mesophase may be easily formed in the molten state by the interaction between mesogenic groups.

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