Glass Transition Temperatures of Poly(alkyl α-Cyanoacrylates)

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Synopsis

The glass transition temperatures of the poly(alkyl α-cyanocrylates) were determined by the dilatometric technique, and some of the values were checked by differential thermal analysis. The data indicate that the T_g's appear to decrease with increase in the size of the alkyl group, for a given molecular weight range. It was also found that the T_g of poly(methyl or butyl α-cyanoacrylate) increased with molecular weight. All cyanoacrylates, excepting methyl and ethyl esters, formed only low molecular weight polymers in aqueous surroundings. Therefore, they have characteristic low glass transition temperatures, causing coalescence at low temperatures.

INTRODUCTION

During the course of an investigation of the hydrolytic degradation of *n*-alkyl α-cyanoacrylates, carried out by heating the polymer powder in water at 100°C, it was noted that some of the cyanoacrylates clumped and formed rubbery masses. Since the degradation rate under heterogeneous conditions such as these is not only expected to be dependent upon the inherent polymer hydrolytic instability but upon surface area as well, it became of interest to determine the glass transition temperatures (T_g) of various of the homologues.

The transition temperatures were determined using both a dilatometric technique and differential thermal analysis, and the results are herein reported.

EXPERIMENTAL

Preparation of Polymer Samples

Anionic Process. Approximately 25 g of the monomer was added to 200 ml water at pH 7.0 dropwise with vigorous stirring. The polymer, which separated as a white powder, was washed with water and a small quantity of methanol and dried under high vacuum at 40°C to constant weight.

Free Radical Process. Benzoyl peroxide (0.2 g) was dissolved in 50 g monomer in a polymer tube which was sealed off under vacuum and heated

at 60°C for 5 hr. The resulting solid polymer was dissolved in nitro-methane, reprecipitated in methanol, and dried under high vacuum at 40°C to constant weight. Solution polymerization was carried out using a 10% solution of the monomer in benzene at the same catalyst concentration and time and temperature conditions as for the bulk polymerization.

Samples of the polymers which were originally in the powder form were compressed in a mold which had been heated to 170°C to make pellets under low pressures. Samples of the bulk-polymerized polymers were in the form of chunks which were used as such.

The number-average molecular weights were determined by using a Mechrolab vapor pressure osmometer, with acetonitrile as a solvent, and intrinsic viscosities were measured by using an Ubbelohde dilution vis-cometer with acetonitrile as solvent.

Preparation of Dilameter

The polymer was cut into small pieces and placed in the bulb of the dilatometer (Fig. 1). The bulb was then sealed to the capillary by means of the ground-glass joint and silicone stopcock grease. Springs were used to prevent leakage and slippage of the joint. One stem of the three-way stopcock was filled with mercury. It was necessary to fill the inner portion of the mercury side of the stopcock to prevent air being forced into the capillary.

The other side of the stopcock was connected to a high-vacuum pump. The system was then evacuated to about 1.5 mm Hg and left there for approximately $1\frac{1}{2}$ hr. After evacuation, the mercury was allowed to flow into the capillary to a height of about 1 cm.

Measurement of Glass Transition Temperatures[2]

The dilatometer was mounted in an oil bath completely surrounding the bulb. The heating element of the bath was regulated to provide a near-constant heating rate of about 1°C per minute. The bath was then heated and readings taken every 3° or 4°C. The mercury level was measured using a cathetometer giving readings to the nearest 0.1 mm. Because of the preparation of the polymers under controlled conditions and the con-stancy of the results obtained in several replicates, the second-order transi-tion temperatures as shown in Figures 2 and 3 for several samples are believed to be real.

RESULTS AND DISCUSSION

The phenomenon of glass transition in polymers is due to the relatively very slow intermolecular motion (below a certain temperature), which increases rapidly above this temperature, causing abrupt changes in the physical properties such as specific volume, specific heat, etc., which are the first derivatives of corresponding thermodynamic functions. The mea-surement of the change in specific volume by the dilatometric technique
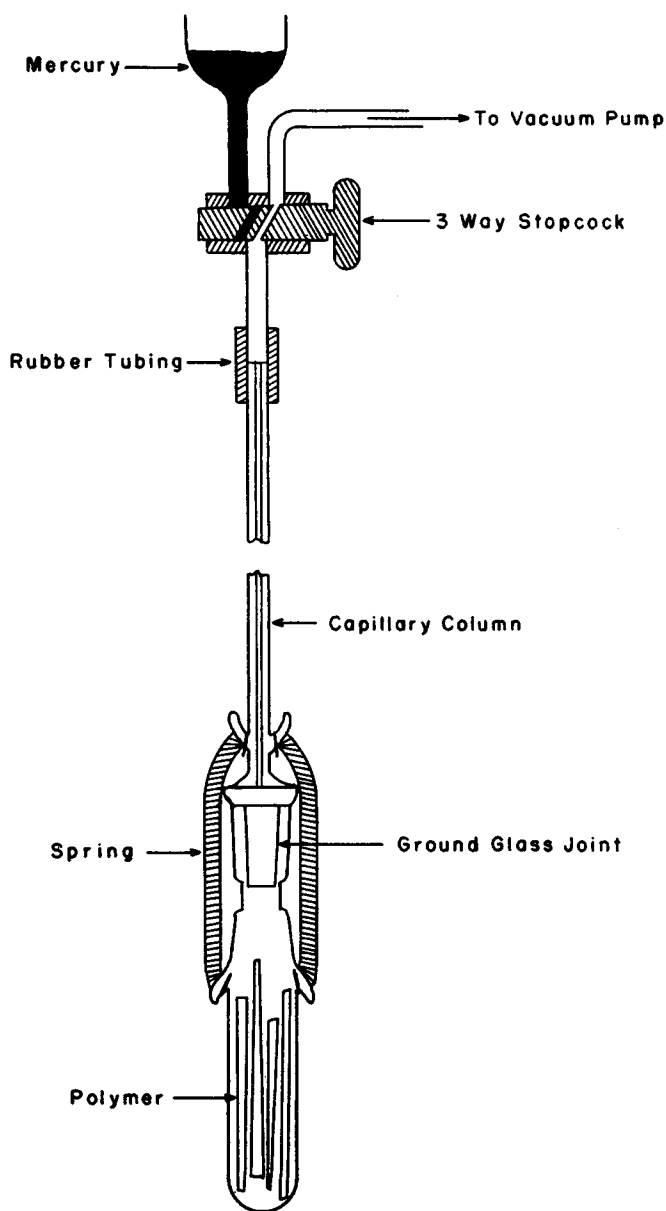
Fig. 1.

was used in the present investigation to find the glass transition tempera-
tures.   Since the coefficient of expansion of mercury is constant over the
temperature ranges used, the changes in the slope of the graph of height of
column against temperature would be due to the change in the state of the
polymer itself.   The glass transitions (T_g) could, therefore, be determined
without the absolute measurements of specific volumes.   The plots of the

TABLE I
Glass Transitions of Poly(alkyl α-Cyanoacrylates)

Monomer	Method of polymerization	T_g, °C Dilato-metric	T_g, °C DTA	M_n	In-trinsic vis-cosity, g/100 ml solu.[a]
1. Methyl α-cyanoacrylate	anionic	100.0		2204	
2. Methyl α-cyanoacrylate	free radicals in solution	125.0	135		0.20
3. Methyl α-cyanoacrylate	free radicals in bulk	160.0			0.6
4. n-Butyl α-cyanoacrylate	anionic	56.0		3820	
5. n-Butyl α-cyanoacrylate	free radicals in bulk	123.0	111.0		3.66
6. Isobutyl α-cyanoacrylate	anionic	51.0		2027	
7. Ethyl α-cyanoacrylate	anionic	115.0		1533	
8. Isopropyl α-cyanoacrylate	anionic	66.0		5960	
9. n-Hexyl α-cyanoacrylate	anionic	86.0		2650	
10. n-Heptyl α-cyanoacrylate	anionic at 25°C[b]	—	88.0		
	at −40°C	—	116.0		

[a] In acetonitrile at 25°C.
[b] In methanol.

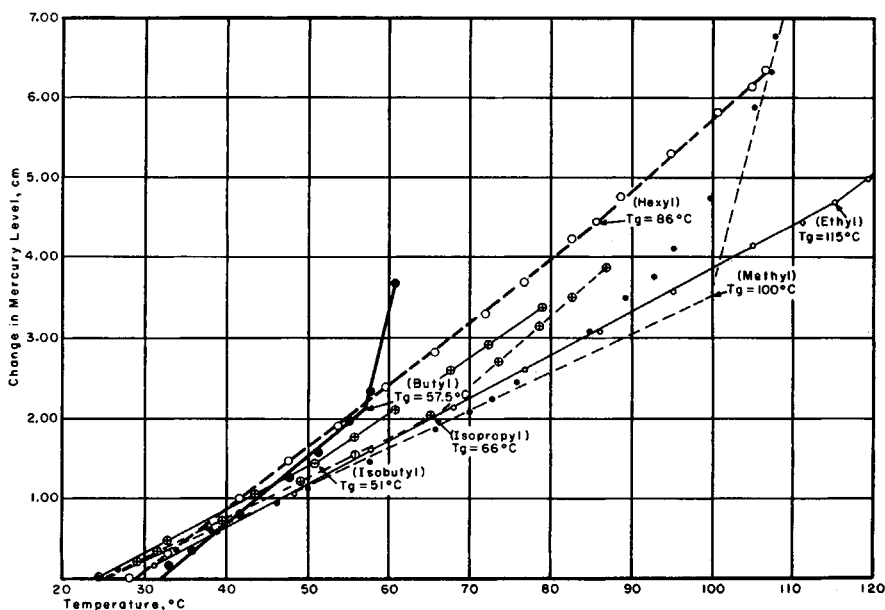GLASS TRANSITION TEMPERATURES OF POLY ALKYL ALPHA CYANOACRYLATES

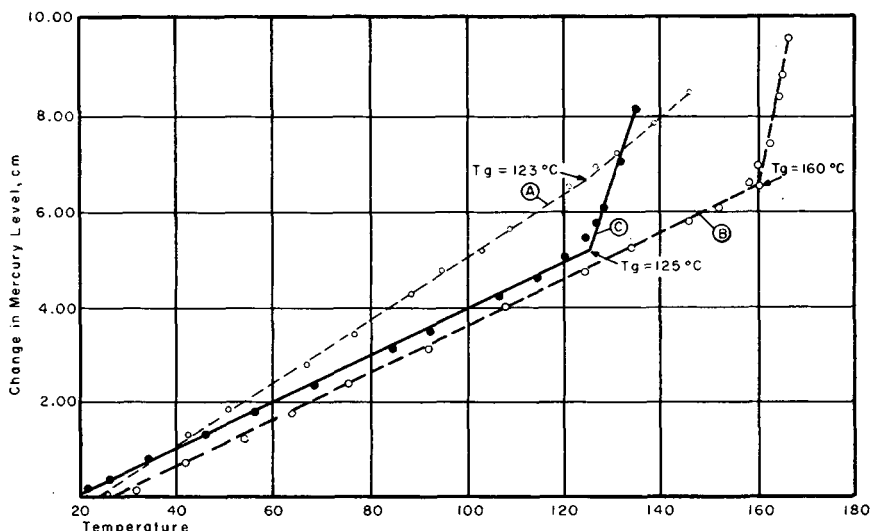Fig. 2. Glass transition temperatures of poly(alkyl α-cyanoacrylates).

Fig. 3. Glass transition temperatures of poly(alkyl) α-cyanoacrylates: Ⓐ poly-(butyl α-cyanoacrylate) (free radical bulk polymerized); Ⓑ poly(methyl) α-cyano-acrylate (free radical bulk polymerized); Ⓒ poly(methyl α-cyanoacrylate (free radical solution polymerized).

heights of mercury column versus the temperatures are given in Figures 2 and 3, and the corresponding T_g's of different polymers are tabulated in Table I.

It may be seen from Table I that the T_g of poly(methyl 2-cyanoacrylate), PMCA, appears to increase with the molecular weight as indicated by an increase in intrinsic viscosity. Although the T_g of PMCA (free radical-polymerized high molecular weight sample) is reported to be indeterminate, owing to the onset of decomposition at 170°C,[3] the present work indicates that T_g is 160°C, somewhat below decomposition temperature, which is in agreement with the Vicat softening points of 165–169°C reported by Kinsinger et al.[4] The anionically polymerized PMCA, as used as tissue adhesives for nonsuture closure of wounds, is of fairly low molecular weight whose T_g is indicated to be 100°C. The solution-polymerized PMCA (a medium molecular weight as shown by intrinsic viscosity) has a T_g of 125°C (Fig. 3). The other homologues which were polymerized by anionic process, by either water or methanol, have a wide range of molecular weights which tend to influence the T_g's[5] along with the structural and physical characteristics. Because it has been shown[6] that the initiating nucleophile used in the anionic initiation of polymerization of the α-cyano-acrylates may enter the growing chain, and because the average molecular weight is low, it is to be expected that the second-order transitions exhibited by these compounds will also be characteristic of their method of prepara-tion. The curves presented in Figures 2 and 3 show definite transition temperatures for the polymers. DTA measurements were carried out for

some of the polymers and the results were in fair agreement with the dilatometric results, as presented in Table I. A Perkin-Elmer differential scanning calorimeter was used for DTA measurements. It is seen that n-butyl, isobutyl, isopropyl, hexyl, and heptyl 2-cyanoacrylates, have glass transition temperatures of less than 88°C, and hence they soften and coalesce to a semisolid mass in hot water, showing little if any degradation to formaldehyde and other products. However, methyl and ethyl α-cyanoacrylates exhibit normal degradation in hot water, until they reach the low molecular weight stage when coalescence occurs.[6] The low second-order transition temperatures of the polymers of higher homologues, formed in aqueous environment, seem to be the major contributing factors for the observed stability of these polymers in the presence of water, along with the intrinsic molecular stability.

SUMMARY

The poly(alkyl α-cyanoacrylates) prepared by anionic initiation in water were of low molecular weight and showed T_g's below 116°C. However, high molecular weight samples prepared by the free-radical process showed higher T_g's. The T_g's of poly(methyl α-cyanoacrylate) and poly(n-butyl α-cyanoacrylate) increased with molecular weight.

References

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