

Dielectric studies on allyl methacrylate-methyl methacrylate copolymers in a slightly polar medium

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Summary

Dielectric constants of allyl methacrylate-methyl methacrylate copolymers are measured in toluene solution at a constant frequency of 2 MHz, within a wide temperature range (20–70°C). Soluble copolymers have been prepared by group transfer copolymerization. Dipole moments are calculated from Guggenheim-Smith equation. The effects of allyl group on the dipole moments of copolymers in a slightly polar medium are discussed.

Introduction

Allyl methacrylate is an important acrylic monomer¹, it has two double bonds in its structure with different reactivities. It has attracted widespread interest from 1930ies. Making use of different reactivities of the two double bonds, initially very low molecular weight soluble product is obtained. The allyl bonds are then activated in order to obtain crosslinked structures. There is little use for brittle and insoluble homopolymers, mainly in thermosets and in vulcanized products. Allyl copolymers have a wider area of use, not only in fields like dental applications and synthetic rubber but also in optical plastics and as dielectric coatings where their dielectric properties are important.

Pollack, Maskat and Strain had obtained polyallyl methacrylate in very dilute solutions at very low conversion without gelation², Blaut and coworkers had obtained prepolymer syrup with photopolymerization without crosslinks³. However Higgins and Weale have shown cyclization in low conversion dilute solution polymerization of allyl acrylate monomers⁴. Linear soluble polyallyl methacrylates have been obtained by anionic methods only.

Group transfer polymerization (G.T.P.) is an ionic living system introduced by Dupont in the 1980 s⁵. In G.T.P. the active end is at the end of the living chain and chain propagates only from that specific point, in our case the vinyl bond. The less active allyl bond does not take part in the reaction so that linear and soluble allyl polymers can be obtained^{6,7}.

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Table.1. Copolymer composition, mean molecular weight per repeat unit and polymer molecular weights of samples.

	<u>Copolymer Composition</u>		<u>Repeat unit</u>	<u>Copolymer</u>
	<u>%allyl</u>	<u>%methyl</u>	<u>molecular weight</u>	<u>molecular weight</u>
M1	-	1.00	100.12	1750
MA10	0.38	0.62	110.08	3850
MA8	0.61	0.38	116.09	3720
MA6	0.88	0.12	123.14	7900
A1	1.00	-	126.16	2000

Although the dielectric properties of vinyl polymers and copolymers have been studied in great detail^{8,18)}, to our knowledge there is not any work on soluble allyl copolymers.

In this work, after preparing soluble allyl methyl copolymers by GTP, their dielectric constants have been measured at 2MHz constant frequency. Within a temperature range (20–70°C). The square of mean dipole moments per repeat unit have been calculated. The variation of $\langle \mu^2 \rangle / x$ with allyl fraction of copolymers at different temperatures is determined.

Experimental

Polymerization

Monomer or monomer mixture (10 mL), The initiator, methyl trimethylsilyl dimethylketene acetal (1-methoxy-2methyl-1-trimethyl silyl-1-propene) (MTS, 0.1 mL) and solvent, tetrahydrofuran (THF, 30 mL) were mixed under dry nitrogen atmosphere. The catalyst, tris (dimethyl amino) sulfonium bifluoride (Tashf₂ as 0.1 M solution in acetonitrile, 1 mL) was then added. The mixture immediately warmed, and after stirring for the required time (according to the desired conversion) the polymer was precipitated into a methanol/water mixture. The polymer was then dried in vacuo at room temperature overnight.

Dielectric Measurements

A WTW model DM01 dipole meter operating at a frequency of 2MHz was used to measure dielectric constants. The measuring cell was a cylindrical gold-plated condenser having a volume of about 20 mL. Its temperature was controlled to $\pm 0.05^\circ\text{C}$ during all measurements. The instrument was calibrated with air and toluene and the calibration checked with other liquids¹⁹⁻²¹⁾. The uncertainties were of the order of 10^{-3} . All the solvents used for calibration and dielectric measurements were middle fractions from two successive distillations. Solutions were made up by weight.

Table 2. The intercept and slope values calculated from dielectric constant versus concentration plots and mean dipole moment square per repeat unit values calculated therefrom at indicated temperatures for homo and copolymers.

Sample	Temp. (°C)	ϵ	$\lim_{w_2 \rightarrow 0} (de/dw_2)$	$(\langle \mu^2 \rangle / x)^*$
M1	20	2.047	3.265	2.806
	25	2.378	3.228	2.875
	30	2.349	3.018	2.784
	35	2.323	2.858	2.730
	40	2.295	2.578	2.549
	45	2.258	2.816	2.882
	50	2.231	2.762	2.926
	60	2.178	2.416	2.738
MA10	20	2.414	1.873	1.769
	25	2.385	1.681	1.645
	30	2.254	1.763	1.788
	35	2.326	1.850	1.942
	40	2.299	1.593	1.732
	45	2.263	1.629	1.832
	50	2.236	1.566	1.824
	60	2.183	1.360	1.694
MA8	20	2.415	1.899	1.893
	25	2.389	1.084	1.119
	30	2.357	1.261	1.349
	35	2.329	1.371	1.519
	40	2.302	1.302	1.493
	45	2.266	1.603	1.903
	50	2.239	1.471	1.807
	MA6	25	2.390	0.730
30		2.361	0.495	0.512
35		2.333	0.683	0.803
40		2.304	0.674	0.820
45		2.226	0.738	0.929
50		2.240	0.750	0.978
60		2.188	0.447	0.623
70		2.133	0.630	0.939
A1	20	2.409	1.323	1.432
	25	2.377	1.426	1.601
	30	2.348	1.493	1.735
	35	2.320	1.246	1.500
	40	2.293	1.156	1.441
	45	2.266	1.114	1.438
	50	2.238	1.200	1.601
	60	2.186	0.947	1.352
70	1.313	1.267	1.934	

*) Dipole moment unit is debye (D)

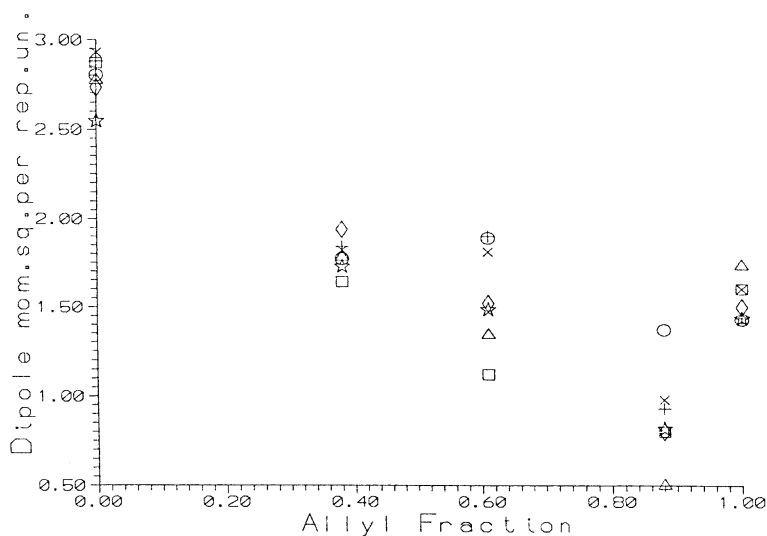


Fig. 1. The variation of dipole moment square per repeat unit with allyl fraction in homo and copolymers, at the indicated temperatures. (20 °C (o), 25 °C (□), 30 °C (Δ), 35 °C (◇), 40 °C (⊕), 45 °C (+), 50 °C (x))

Results and Discussion

The compositions of copolymers were taken from Çatalgil-Giz and Öncül-Koç²²⁾. The reactivity ratios of methyl methacrylate and allyl methacrylate monomers $r_{\text{allyl}} = 1.60 \pm 0.29$, $r_{\text{methyl}} = 0.34 \pm 0.05$ ²²⁾. Copolymer compositions, mean molecular weights per repeat unit and polymer molecular weights are given in Table. 1.

Dielectric constants of copolymers were measured over a wide range of temperatures from 20–70°C. The mean square dipole moments per repeat unit in the copolymer chain $\langle \mu^2 \rangle / x$ were calculated from the Gugenheim-Smith equation²³⁻²⁴⁾.

$$\frac{\langle \mu^2 \rangle}{x} = \frac{27 k T M_0}{4\pi N_A \rho_1} \left[\frac{\frac{d\epsilon}{dw_2}}{(\epsilon_1 + 2)^2} - \frac{\frac{dn^2}{dw_2}}{(n_1^2 + 2)^2} \right]$$

In the above equation k is the Boltzmann constant, T is the absolute temperature, N_A is Avogadro's number, M_0 is the molar weight of a repeat unit, x is the number of repeat units in the chain ρ_1 , ϵ_1 and n_1 are the density, dielectric constant and refractive index of pure solvent respectively, w_2 is the weight fraction of the polymer, $d\epsilon/dw_2$ the dielectric constant increment and dn^2/dw_2 the refractive index increment. From the variation of dielectric constants of homo and copolymers of allyl methacrylate (AMA) and methyl methacrylate (MMA) in toluene solution with temperature, concentration and composition, the intercept ϵ and slope $\lim_{w_2 \rightarrow 0} (d\epsilon/dw_2)$ values obtained by linear least square fit

and $\langle \mu^2 \rangle / x$ values are given in Tab.2. Values of the variation of the refractive index with concentration given in literature for polymethyl methacrylate and polyethyl methacrylate in toluene are at least an order of magnitude less than the value of the $d\varepsilon/dw_2$, given here and they have been neglected¹¹⁻¹⁷.

The dipole moments obtained for PMMA in toluene are greater than the values quoted for these polymers in benzene¹⁰. Since toluene is slightly polar and each MMA unit displaces a toluene molecule and its dipole moment, the excluded volume effect would tend to give a lower value for the measured $\langle \mu^2 \rangle / x$. These results indicate that polymer unit solvent interaction is strong and that it dominates the excluded volume effect in our case.

Hindrance to free rotation decreases with increasing temperature. As dielectric measurements at a given frequency "see" the dipole moment that is aligned with the field at that frequency, the hindrances decrease the observed dipole moment and increased mobility at higher temperatures increases the dipole moment seen. The variation of $\langle \mu^2 \rangle / x$ with allyl fraction of homo and copolymers at different temperatures is given in Fig. 1. This result also verifies the above consideration and from methyl to allyl $\langle \mu^2 \rangle / x$ values decrease slightly. The dip that can be seen at %88 allyl %12 methyl (MA6) appears at all temperatures. Further work is in progress to determine whether it is an experimental fluctuation or an effect caused by molecular conformations.

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