

Dynamic Mechanical Behavior of Chlorosubstituted Derivatives of Poly(ethyl Methacrylate) and Poly(ethyl Acrylate)

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Synopsis

A freely oscillating torsional pendulum was used in the investigation of the influence of trichloroethyl, tetrachloroethyl, trichloromethoxyethyl, and trichloroethoxyethyl side groups on the molecular mobility in the glassy state and on the glass transition temperature of poly(meth)acrylates. All the polymers under study, which may be used as fire retardants, exhibit a simple relaxation behavior. While the parameters of the low-temperature and secondary relaxation process in the glassy state are not noticeably affected by the substituents used, the glass transition temperature T_g , increases with rising polarity and volume of side chains. The increase is larger in the series of polyacrylates, so that differences in the softening temperatures of polymethacrylates and polyacrylates having the same side chains decrease considerably with growing substitution.

INTRODUCTION

Polyacrylates and their derivatives rank among those polymers for which the effect of the bulkiness, shape, and polarity of substituents on molecular mobility has been studied systematically. Cl— and —C≡N groups appear quite commonly, along with CH₃, as substituents R_1 in the monomer CH₂=C(R_1)—COOR₂, i.e., in the α -position on the main chain.¹⁻³ In addition to alkyl groups of various size and branching,^{1,4-6} hydroxyalkyls,^{7,8} a number of fluorinated alkyls,⁴ and chloro-, bromo-, and cyanoethyl groups⁹ have been employed as the side groups R_2 . Recently, tri- and tetrasubstituted chloro derivatives of ethyl acrylate and ethyl methacrylate have been prepared,¹⁰⁻¹³ which may serve as fire retardants. The resulting polymers represent a complete series of model compounds, which allows us to supplement earlier results concerning the molecular mobility of polymethacrylates. This paper deals with the determination of their molecular mobility and main (glass) transition temperature T_α by means of dynamic mechanical measurements.

The initial polymers, poly(ethyl methacrylate) (PEMA) and poly(ethyl acrylate) (PEA), also exhibit, in addition to the main (α) transition at 78°C (1 Hz),¹⁴ or -24°C (1 Hz),^{5,15,16} secondary transitions (relaxation, dispersion), generally attributed to the relaxation motions of the side groups. A secondary (β_1) transition assigned to the hindered rotation of the —COOC₂H₅ groups has been observed,¹⁴ with PEMA at about 10°C (1 Hz) and PEA¹⁵ at -120°C (1 Hz). The cause of the substantially higher T_α and T_{β_1} of PEMA is related to the presence of α -methyl groups, which generally reduce the flexibility of main chains and impede the rotation of —COOR₂ groups. Molecular motions underlying β_1 relaxation of polymethacrylates and polyacrylates are different, however, since the magnitude of the β_1 maximum of polyacrylates is much smaller and two loss

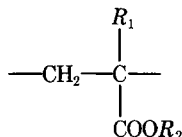
maxima appear in the copolymers of methacrylate and acrylate with the same group R_2 ; the intensity of these maxima is proportional to the volume fraction of the respective component.^{14,17} The rotational motion of the ethyl groups of PEMA gives rise to the low-temperature (γ) dispersion^{18,19} at about -230°C (1 Hz). The γ dispersion has also been identified by dielectric²⁰ and nmr measurements,^{21,22} similarly to the β_1 dispersion.

Of chlorinated derivatives of PEMA, poly(2-chloroethyl methacrylate)^{2,9} was investigated by means of dynamic mechanical measurements; the main transition temperature of poly(2,2,2-trichloroethyl acrylate)¹⁶ was found to be $T_\alpha = 55^\circ\text{C}$ (60 Hz). The dielectric properties of poly(2-chloroethyl acrylate) and of a series of polymethacrylates with the side group $-(\text{CH}_2)_n-\text{Cl}$ for $n = 1$ to 4 were also investigated.²³ Poly(2-chloroethyl methacrylate) exhibits the transition temperatures $T_\alpha \approx 65^\circ\text{C}$ (1 Hz) and $T_\gamma = -156^\circ\text{C}$ (1 Hz), which are 15 or 32°C higher than those of poly(n -propyl methacrylate).^{7,9,14} (The β_1 loss maximum is indistinct for both polymers, owing to the overlapping with the α maximum.) These shifts are due to the polarity of the chloroethyl side group, because the methyl group and the chlorine atom have an almost identical van der Waals radius,¹ so that steric hindrances of the molecular motion brought about by side chains are very similar in both polymers. From this viewpoint, too, it was regarded as useful to examine the effect of multiple substitution with chlorine—sometimes combined with alkoxy—on the molecular mobility of poly(meth)acrylates.

EXPERIMENTAL

The synthesis of monomers and their polymerization have been described earlier.¹⁰⁻¹³ The following polymers were prepared (Table I); poly(ethyl methacrylate) (PEMA), poly(2,2,2-trichloroethyl methacrylate) (P3ClEMA), poly(1,2,2,2-tetrachloroethyl methacrylate) (P4ClEMA), poly(2,2,2-trichloro-1-methoxyethyl methacrylate) (P3ClEMEMA), poly(2,2,2-trichloro-1-ethoxyethyl

TABLE I
Parameters of α and β_1 Dispersions of Chlorosubstituted Poly(meth)acrylates



Sample	R_1	R_2	$T_\alpha, ^\circ\text{C}$	G_α^c, MPa	$T_{\beta_1}, ^\circ\text{C}$	$G_{\beta_1}^c, \text{MPa}$
PEMA	CH_3	CH_3-CH_2	77	49	0	86
P3ClEMA	CH_3	$\text{Cl}_3\text{C}-\text{CH}_2$	99	118	0	38
P4ClEMA	CH_3	$\text{Cl}_3\text{C}-\text{CHCl}$	97	140	-2	48
P3ClEMEMA	CH_3	$\text{Cl}_3\text{C}-\text{CH}(\text{OCH}_3)$	122	94	-2	46
P3ClEEMA	CH_3	$\text{Cl}_3\text{C}-\text{CH}(\text{OC}_2\text{H}_5)$	126	93	0	47
P3ClEA	H	$\text{Cl}_3\text{C}-\text{CH}_2$	41	150	(-160)	(36)
P4ClEA	H	$\text{Cl}_3\text{C}-\text{CHCl}$	70	140	-130	32
PEA ^c	H	CH_3-CH_2	-24		(-145)	—

^a Dispersion temperature read for the peak of the loss maximum (1 Hz).

^b Height of the loss maximum.

^c Data taken from Refs. 5, 15, and 16.

methacrylate) (P3ClEEMA), poly(2,2,2-trichloroethyl acrylate) (P3ClEA), and poly(1,2,2,2-tetrachloroethyl acrylate) (P4ClEA). Samples for dynamic mechanical measurements were prepared by crosslinking copolymerization using 0.5 wt. % ethylenedimethacrylate as the crosslinking agent. The monomers were diluted with cyclohexanone to the concentration 60 vol %, so that during the polymerization (between plane-parallel glass plates) the glass transition temperature was not achieved before complete conversion of monomers; furthermore, the cutting out of the samples was facilitated, because the polymers were very brittle in the glassy state. The radical polymerization initiated by approximately 0.1 wt. % azo-bis-isobutyronitrile (related to the monomer) proceeded at 65°C for 7 hr. The cut-out samples, $70 \times 7 \times 1 \text{ mm}^3$ in size, were extracted for 2 weeks in an excess of a fresh ethanol-dioxan mixture (3:2) in order to remove the diluent and the monomer and initiator residues. The samples were then dried to constant weight at about 80°C in the vacuum of a rotary oil pump. Before measurement of the dynamic mechanical properties, the samples were heated to the softening temperature and slowly cooled to room temperature. The temperature dependence of the components of the complex shear modulus was determined by means of a freely oscillating torsional pendulum (about 1 Hz) with digital recording of oscillations. The temperature of measurement was continuously increased at a rate of 1°C/min from the liquid nitrogen temperature to the softening temperature of the samples.

RESULTS AND DISCUSSION

The temperature dependence of the storage and loss moduli of PEMA (Fig. 1, Table I) is identical with the dependence given in the literature^{1,14} for a radical-polymerized specimen. The existence of a low-temperature maximum below the liquid nitrogen temperature is indicated by a decrease in the loss modulus between -195 and -175°C. A narrow plateau of the loss modulus at temperatures about -110°C, also observed in Ref. 14, is probably caused by traces of low-molecular-weight compounds. The peak of the broad secondary β_1 maximum is located at 0°C, that is, at a temperature 10°C lower than mentioned in

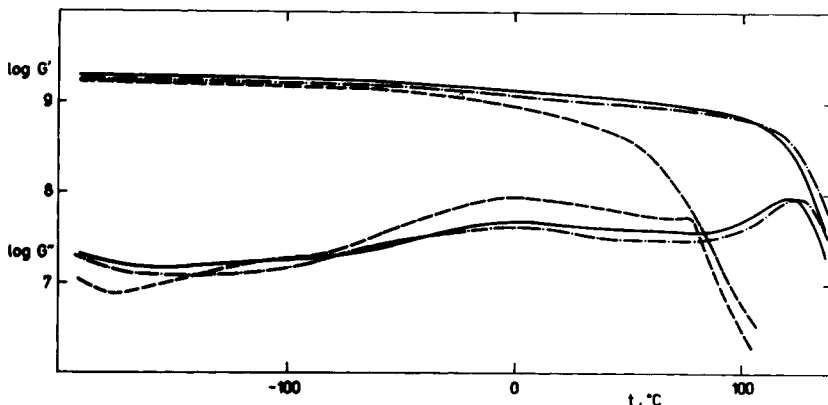


Fig. 1. The temperature dependence of the storage (G') and loss shear (G'') moduli (Pa) of poly(ethyl methacrylate) (---), poly(2,2,2-trichloro-1-methoxyethyl methacrylate) (—) and poly(2,2,2-trichloro-1-ethoxyethyl methacrylate) (-·-·).

the literature.^{1,14,15} On the other hand, the α maximum is rather unpronounced, but $T_\alpha = 78^\circ\text{C}$ (1 Hz) is in good agreement with earlier data.^{1,14} The reference sample of poly(ethyl acrylate) was not available, and Table I contains only data reported in the literature.^{5,15,16}

It is known that substitution of the ethyl side group with a propyl, chloroethyl, or hydroxyethyl group in polymethacrylates causes the γ maximum to shift from -230°C to a temperature near -175 , -156 , or -133°C , respectively. We therefore expected that the γ process of PEMA derivatives under study would occur above the liquid nitrogen temperature. It was found, however, that at the frequency of 1 Hz, none of the chlorosubstituted derivatives of either PEMA or PEA exhibited the γ maximum above -196°C (Figs. 1–3). One may infer from the decrease in the loss modulus G'' of the substituted PEMAs in the range from -196 to -160°C that the γ process was not eliminated by the introduction of chlorine atoms, but was preserved at temperatures close to the T_γ of PEMA. It seems noteworthy that neither P3ClMEMA nor P3ClEEMA exhibit the γ dispersion in the temperature range under investigation, although poly(methoxyethyl methacrylate) is characterized by a distinct loss maximum²⁴ at -140°C . The effect of the substituents R_2 on the γ dispersion of polymethac-

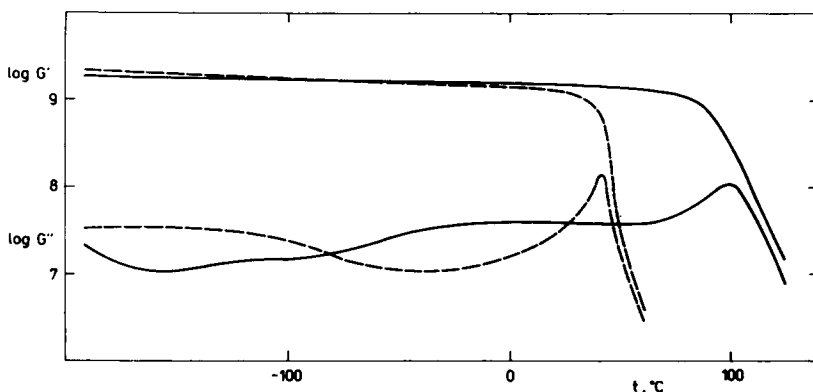


Fig. 2. The temperature dependence of the storage (G') and loss shear (G'') moduli (Pa) of poly(2,2,2-trichloroethyl methacrylate) (—) and poly(2,2,2-trichloroethyl acrylate) (---).

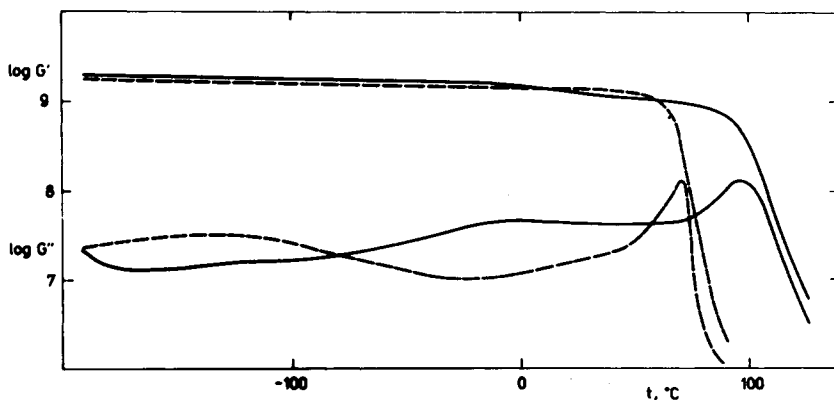


Fig. 3. The temperature dependence of the storage (G') and loss shear (G'') moduli (Pa) of poly(1,2,2,2-tetrachloroethyl methacrylate) (—) and poly(1,2,2,2-tetrachloroethyl acrylate) (---).

rylates cannot be elucidated without dynamic mechanical and, if necessary, dielectric measurements encompassing the entire temperature interval of dispersion.

Neither do bulky substituents in the side chain of polymethacrylates appreciably affect the parameters of β_1 dispersion (Table I). The height of the β_1 maximum remains approximately the same and corresponds to half the height of the loss maximum of PEMA. Temperature T_{β_1} of all polymethacrylates taken for investigation is identical, which is in agreement with earlier conclusions^{1,7,14,15} that this temperature is generally independent of the magnitude of the substituent attached to the oxycarbonyl group. The β_1 maximum of PEA derivatives (Figs. 2 and 3) is very flat, so that the temperature position of this process can be determined only approximately (Table I). It is clear, nevertheless, that T_{β_1} of the polyacrylates is more than 100°C lower than that of the polymethacrylates with an identical side chain. Such a difference between the secondary dispersion temperatures of analogous polyacrylates and polymethacrylates has also been observed earlier.^{14,15,17} The results shown in Table I indicate that the substituents used also have little effect on the extent of the side-chain relaxations in the case of acrylate polymers, even though the character of relaxation motions of side chains differs from that of polymethacrylates.

As expected, the introduction of bulky and polar substituents into the side chain of PEMA or PEA leads to an increase in the glass transition temperature; however, differences or relations between the T_α 's indicate a complex combining of the effects of polarity and steric hindrances (Table I). While the T_α of PEMA is 77°C, and is reduced to 65°C by the introduction of one chlorine atom,⁹ the introduction of an additional two chlorine atoms into position 2 on the ethyl group accounts for an increase in T_α to 99°C (1 Hz). The fourth chlorine atom (in position 1) has virtually no further effect on the glass transition temperature (although the polymer becomes extremely brittle). On the other hand, the substitution of hydrogen with methoxy or ethoxy group (in position 1) produces a much larger rise—to 122 and 126°C, respectively—in the glass transition temperature. This effect may be attributed to a decrease in the mobility of segments of the main chains owing to increasing steric hindrances, because the polarity of the polymer is raised by the introduction of the fourth chlorine atom.

The introduction of three or four chlorine atoms into the side chain of poly(ethyl acrylate) results in a considerably larger rise in T_α 's than in the series of polymethacrylates, e.g., T_α of P4ClEA is higher by 29°C than that of P3ClEA, and this in turn has a T_α 65°C above that of PEA (Table I). Owing to the increase in the glass transition temperature of polyacrylates with increasing number of chlorine atoms, differences between polyacrylates and polymethacrylates with identical side chains become smaller. While the difference between the T_α of PEMA and PEA is about 100°C [which is the usual difference between the glass transition temperatures of analogous poly(alkyl methacrylates) and poly(alkyl acrylates)^{1,4,5,17}], the T_α of P4ClEMA is only 27°C higher than that of P4ClEA.

It can be summarized that the substitution of the ethyl side group by the $\text{Cl}_3\text{C}-\text{CH}_2-$ or $\text{Cl}_3\text{C}-\text{CHCl}-$ has little influence on the molecular mobility below the glass transition temperature. The relaxation patterns remain very simple and rather similar (except for the marked rise in T_α), even after the in-

roduction of side groups $\text{Cl}_3\text{C}-\text{CH}(\text{OCH}_3)-$ or $\text{Cl}_3\text{C}-\text{CH}(\text{OC}_2\text{H}_5)-$. The most significant effect associated with the introduction of the bulky and polar side substituents is a rise in the glass transition temperature, particularly so for the polyacrylates. As regards the intensity of relaxation processes, the influence of substituents is that while for PEMA $G''_{\beta_1} > G''_{\alpha}$ (Table I), a reciprocal relation holds for all the other polymers.

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