Macromolecules 1992, *25*, 6563–6567

Dielectric Relaxations of Poly(fluoroalkyl methacrylate)s and Poly(fluoroalkyl α-fluoroacrylate)s

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Received March 11, 1992; Revised Manuscript Received August 10, 1992

ABSTRACT: Dielectric relaxation studies were made on two homologous series of poly(fluoroalkyl methacrylate) (PFM) and poly(fluoroalkyl α-fluoroarylate) (PFF). In both series there were observed α above T_g and γ relaxations below T_g, which are assigned to reorientational motion of long segments and local molecular motion of fluoroalkyl side groups, respectively. As the length of the fluoroalkyl side groups are longer, the α relaxation gradually shifted to lower temperatures and the γ relaxation rapidly moved to higher temperatures, being very consistent with the well-known results in the homologous series of poly(alkyl methacrylate). However, the α relaxation was much larger in PFF than in PFM, which was explained by the polar nature of the α-C–F bond in the main chain, while the magnitude of the γ relaxation was affected sensitively by the polarity of the fluoroalkyl side groups.

Introduction

Recently, several fluoroalkyl acrylate and methacrylate polymers have been developed and their physical properties have been studied by several workers.[1-4] Poly(fluoroalkyl acrylate)s (PFA), poly(fluoroalkyl methacrylate)s (PFM), and poly(fluoroalkyl α-fluoroacrylate)s (PFF) have been found to be transparent, low refractive index, and low surface tension polymers. Taking advantage of these useful physical properties, several derivatives of the polymers have been industrially used as clad material for optical fibers, high-sensitive resist polymers for microlithography,[5] moisture-proof coating agents, oil and water repellent agents, and so on.[6] Moreover it has been found that the long fluoroalkyl side groups were crystallized in the polymer matrix to form intermolecular packings similar to those in the crystallites of polytetrafluoroethylene and, as a whole, a layer structure by the fluoroalkyl groups whose layer thickness is comparable to the length of the fluoroalkyl groups.

The structural and physicochemical features mentioned above are considered to be rather novel in the polymeric materials. It is, therefore, worthwhile to study various physical properties and clarify reason for the appearance of novel properties. Generally, dielectric relaxations faithfully reflect the segmental molecular motion of polymers through polar groups of segments as the indicator. Therefore, dielectric relaxation studies should provide us new information on relationships between structure and physical properties in polymers. To date, a lot of dielectric studies have been extensively made for alkyl acrylate and alkyl methacrylate polymers[7,8] but unexpectedly not reported for the corresponding fluoroalkyl polymers, to our knowledge. In this paper, we report dielectric relaxations of PFM and PFF homologues. It is discussed how the segmental molecular motion changes by the introduction of a F atom to acrylate polymers.

Experimental Section

Fluoroalkyl α-fluoroacrylates (monomers) were prepared by a dehydrogen chloride reaction of α-fluoroacryl chloride and the corresponding fluoro alcohol; α-fluoroacryl chloride (1.0 mol)[9] was added dropwise to a mixture of fluoroalkyl alcohol (1.1 mol), triethylamine (1.0 mol), and hydroquinone (0.01 mol) in an iced bath.[2] After the reaction solution was washed by chilled water and chilled 5% $NaHCO_3$ alternately, it was distilled under reduced pressure to obtain the products (yield is 70%). Poly(fluoroalkyl methacrylate)s (PFM) and poly(fluoroalkyl α-fluoroacrylate)s (PFF) were prepared by bulk polymerizations; the mixture of monomer (10 g), AIBN as the initiater (0.0015 g), and 1-dodecanethiol as chain transfer agent of the chain reaction (0.138 g) was sealed into a Pyrex tube after deaerating under liquid nitrogen, and then the bulk polymerization was performed at 333 K for 60 h. The polymers obtained were fully dried in vacuo at 443 K and then were compression molded into sheets at 503 K under 10 kg cm^{-2} load. All the samples used here are listed in Table I.

Characterizations of PFF and PFM were performed by ^{19}F NMR and ^{1}H NMR spectroscopy. Here, ^{19}F NMR spectra were measured in $(CH_3)_2CO/CH_3Cl$ solvent using TFA as a standard by use of a JEOL FX-100 spectrometer (93.7 MHz), and ^{1}H NMR spectra, in $(CD_3)_2CO/CD_3Cl$ solvent using TLC as a standard by use of a Burker AC-300P spectrometer (300. 13 MHz). Both ^{19}F NMR and ^{1}H NMR showed the characteristic absorptions for PFM and PFF.

Figure 1 shows ^{19}F NMR spectra of the α-F region in the main chains of PFF and ^{1}H NMR spectra of the α-CH_3 region in the main chains of PFM. In ^{19}F NMR, there are observed three splitting peaks around 84, 88, and 92 ppm which are related to a triad stereoregularity, namely isotactic triad (mm), heterotactic triad (mr), and syndiotactic triad (rr), respectively, according to the assignments of Majumder et al.[10] and other workers.[11] The triad stereoregularity of PFM was also estimated from the ratio in intensity between three splitting peaks of α-CH_3 of the main chains. The stereoregularities obtained are listed in Table I. The data suggest that PFF homologues are a little more isotactic than PFM homologues.

Dielectric measurements were carried out with a multifrequency LCR meter (Yokogawa-Hewlett Packard, Type 4274A) in a temperature range 90–450 K at several frequencies between 100 Hz and 100 kHz. The three terminal electrode system was used as previously described.[12] The electrode system was constructed by the main and unguarded disk electrodes, where the main electrode was electrically guarded by a cocentric guard ring. The outer diameter of the main electrode was 37 mm, and

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0024-9297/92/2225-6563$03.00/0

Table I
Lists of Poly(fluoroalkyl methacrylate)s (PFM) and Poly(fluoroalkyl α-fluoroacrylate)s (PFF)

sample	alkyl group	triad stereoregularity mm	mr	rr	density (g cm^{-3}) at 298 K	T_g (K)	intrinsic viscosity (dL g^{-1})	weight av MW (×10^5)
P3FM	$-CH_2-CF_3$	0.0693	0.407	0.524	1.4531	355	0.63	4.6
P4FM	$-CH_2-CF_2-CF_2H$	0.069	0.376	0.555	1.4960	353	0.47	4.7
P5FM	$-CH_2-CF_2-CF_3$	0.056	0.406	0.538	1.5204	350	1.41	22.5
P8FM	$-CH_2-(CF_2)_3-CF_2H$	0.059	0.418	0.522	1.6382	320	1.37	7.6
P17FM	$-(CH_2)_2-(CF_2)_7-CF_3$				1.7427	310	0.48	
P3FF	$-CH_2-CF_3$	0.13	0.48	0.39	1.5868	398	0.40	1.9
P4FF	$-CH_2-CF_2-CF_2H$	0.12	0.48	0.40	1.6447	368	0.47	2.2
P5FF	$-CH_2-CF_2-CF_3$	0.12	0.48	0.40	1.6540	374	0.58	2.0
P8FF	$-CH_2-(CF_2)_3-CF_2H$				1.7588	338	0.25	1.7
P17FF	$-(CH_2)_2-(CF_2)_7-CF_3$				1.8192	388		

Table II
Relaxation Parameters for α and γ Relaxations

sample	α relaxation T_{max} (K) at 1 kHz	T_o	A	B	C_{1g}	C_{2g}	f_g	γ relaxation T_{max} (K) 1 kHz	ΔH (kJ mol^{-1})
P3FM	378	289	11.7	768	11.6	66	0.037		
P4FM	380	268	11.4	965	11.4	85	0.038	140	30
P5FM	374	218	16.3	2070	15.7	132	0.028	120	20
P8FM	357	241	11.2	950	12.0	79	0.036	155	42
P17FM	369[a]							158	36
P3FF	443[b]								
P4FF	407	270	13.3	1407	14.4	98	0.030	150	33
P5FF	435[b]							125	23
P8FF								150	39
P17FF	409	336	11.4	619	11.9	52	0.036	159	33

[a] T_{max} at 30 kHz. [b] T_{max} at 10 kHz.

those of the guard ring and the unguarded electrode were 50 mm. The gap between the main and guard ring was 1 mm. The disk sample, whose diameter and thickness were 50 mm and about 0.5 mm, respectively, was mounted between the main and unguarded electrodes. The electrical contact between the sample faces and the electrodes was ensured by depositing aluminum on the sample surfaces. The geometric capacitance was estimated by the sample thickness and the area of the main electrode. Thermal expansions were measured at a heating rate of about 0.3 K min^{-1} by use of a glass tube dilatometer, in which the sample was immersed in liquid Hg to avoid a formation of voids on the surface of the sample. The change in volume of the sample with temperature was calculated from the reading of the height of Hg in the 0.6-mm-i.d. capillary of the diameter. The specific volume at 298 K was obtained by a buoyancy method with benzene.

Results and Discussion

Alkyl acrylate and alkyl methacrylate polymers are typical side-chain containing polymers, and hence these dielectric and mechanical relaxation studies have received much attention from many scientists to clarify the relationships between structure and physical properties. In dielectric relaxation studies,[7,8] poly(alkyl methacrylate)s exhibit the α, β, and γ relaxations at decreasing temperatures, which are assigned respectively to a reorientational motion of long segments containing backbone chains above T_g, a hindered rotational motion of –COOR groups about the C–C bond which links them to the main chains, and a local molecular motion of alkyl groups in the side chains. As the length of the alkyl group is longer, the α relaxation shifted to lower temperatures due to a plasticizing effect of alkyl groups and the γ relaxation, reversely to higher temperatures, while the β relaxation lay at almost the same temperature, independent of the length of alkyl group. As a result, the α and β relaxations merged in the higher alkyl homologues.

Figure 2 shows the temperature dependence of dielectric loss, ε″, for P4FM at several frequencies. There are two observed relaxations near 400 and 150 K which are assigned to α and γ relaxations, respectively, as are later described. Temperature dependences of dielectric loss (ε″) at 10 kHz are illustrated respectively in Figure 3 for PFM homologues and in Figure 4 for PFF homologues. The α and γ relaxations are observed in all the samples, although the γ relaxation is only seen as a skirt near 90 K for P3FM and P3FF. Figure 5 shows Arrhenius plots of α and γ relaxations for all the samples.

As the length of the fluoroalkyl group is longer, the γ relaxation shifts to higher temperatures and the α relaxation moves somewhat to low temperatures. The Arrhenius plots of the α relaxation are curved and were analyzed by a modified Arrhenius equation

$$\log f = A - B/(T_m - T_o) \quad (1)$$

where f and T_m are the measuring frequency and the relaxation temperature, respectively, and A, B, and T_o are parameters determined by trial and error so as to obtain the best fit with the experimental curve. The WLF constants (C_{1g} and C_{2g}) and the free volume fraction at T_g (f_g) were obtained by applying the above parameters and T_g to the WLF equation. The relaxation parameters are listed in Table II. The values of f_g lie around 0.03 for all the samples, which suggests that the α relaxation obeys the WLF equation. On the other hand, the Arrhenius plots of the γ relaxation are linear and so obey the Arrhenius equation. The activation enthalpy changes (ΔH) for the γ relaxation were estimated to be between 20 and 42 kJ mol^{-1} (Table II), and these small values indicate that the γ relaxation is related to a local molecular motion of short segments. Consequently, according to the assignments for the relaxations in poly(alkyl methacrylate)s, the α relaxation is assigned to a reorientational motion of long segments containing backbone chains above T_g, although it could merge with the β relaxation (the rotational motion around the C–COOR bond), while the γ relaxation is attributed to a local molecular motion of fluoroalkyl groups below T_g.

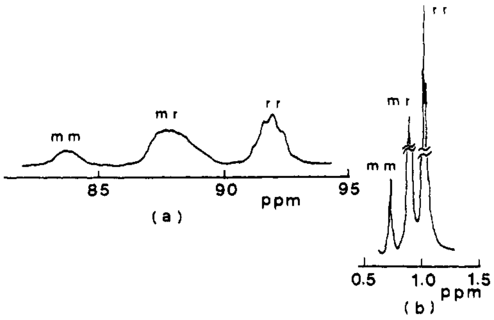

Figure 1. (a) ^{9}F NMR spectra in α-F region of P4FF and (b) ^{1}H NMR spectra in α-CH$_3$ region of P4FM.

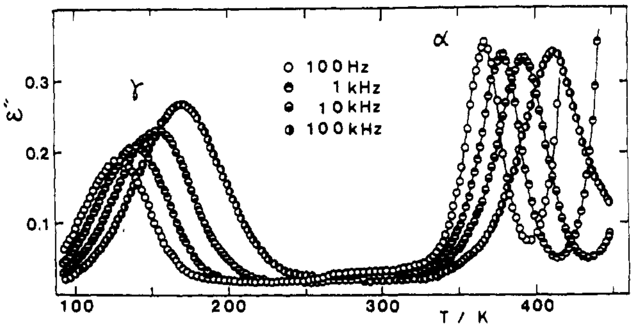

Figure 2. Temperature dependence of dielectric loss (ϵ'') for P4FM at several frequencies.

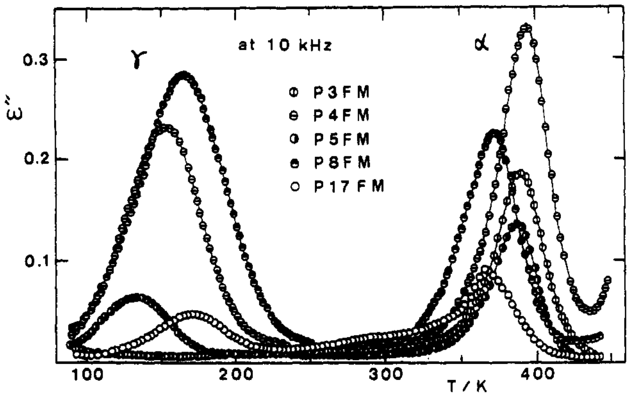

Figure 3. Temperature dependences of dielectric loss (ϵ'') for PFM homologues at 10 kHz.

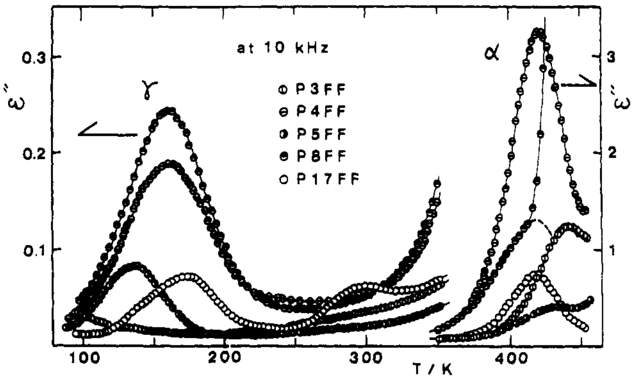

Figure 4. Temperature dependences of dielectric loss (ϵ'') for PFF homologues at 10 kHz.

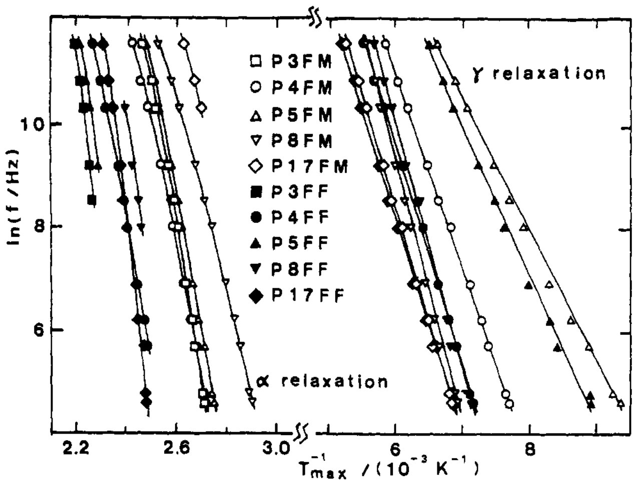

Figure 5. Arrhenius plots of α and γ relaxations.

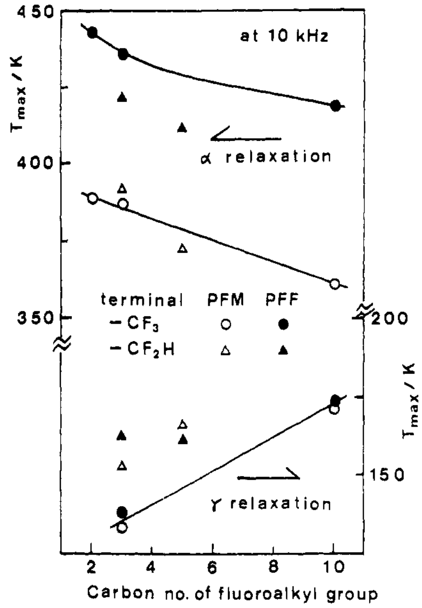

Figure 6. Plots of relaxation temperature (T_{max}) versus carbon number of the fluoroalkyl group (n).

In Figure 6, T_{max} values at 10 kHz are plotted against the carbon number of the fluoroalkyl group (n). With increasing n, T_{max} decreases for the α relaxation and inversely increases for the γ relaxation, as described already. In the α relaxation, T_{max} as well as T_g (Table I) are by about 50 K higher in PFF than in PFM. In poly(alkyl acrylate)s and poly(alkyl methacrylate)s, the effect of stereoregularity on dielectric relaxation behavior has been studied.[13,14] Briefly speaking, the α relaxation was located at lower temperatures in the isotactic configuration than in the atactic configuration. Since the isotacticity is somewhat larger in PFF homologues than in PFM homologues (Table I), the difference in T_{max} between the two homologues may be related not to the stereoregularity but to the stiffness of the backbone chains. Mikhailov and Borisova[15] found that the dielectric α relaxation appears at considerably higher temperatures for poly(methyl α-chloroacrylate) than for poly(methyl methacrylate), although the van der Waals radius of a Cl atom is approximately equal to that of a CH$_3$ group, and explained this change by the difference in polarity between C–Cl and C–CH$_3$ bonds. Consequently, the polar α-F substituent would increase the stiffness of the main chains more than the nonpolar α-CH$_3$ substituent. In each homologous series, T_{max} (T_g) decreases with increasing n, which is generally understood by a plasticizing effect of the long alkyl side groups. However, the decrease for both PFM and PFF homologues is not so large as that for the corresponding poly(alkyl methacrylate)s[5] and this may be related to a rigidity of the fluoroalkyl groups. On the other hand, T_{max} for the γ relaxation increases with increasing n but is scarcely affected by the α-substituents of the main chains. This result indicates that the γ relaxation is due to the molecular motion of the fluoroalkyl

Table III
Values of Static Dielectric Constant (ϵ_0), High-Frequency Limiting Dielectric Constant (ϵ_∞), Dielectric Increment ($\Delta\epsilon$), Dipole Moment (μ), and the Cole–Cole Distribution Parameter of Relaxation Time (β) for γ Relaxation and the Calculated Dipole Moment (μ_{cal}) for Several Fluoroalkanes

sample	T (K)	ϵ_0	ϵ_∞	$\Delta\epsilon$	β	μ (D)
P3FM	94	3.030	2.796	0.234	0.26	0.231
P4FM	140	4.367	2.617	1.750	0.30	0.810
P5FM	131	3.021	2.632	0.389	0.40	0.401
P8FM	150	5.377	2.571	2.806	0.22	1.226
P17FM	170	2.700	2.382	0.318	0.38	0.635
P3FF	95	3.499	3.235	0.264	0.41	0.218
P4FF	171	4.243	2.635	1.608	0.34	0.827
P5FF	131	3.275	2.673	0.602	0.32	0.474
P8FF	149	4.737	2.466	2.271	0.25	1.102
P17FF	159	3.545	3.089	0.456	0.34	0.626

compd	chem formula	μ_{cal} (D)
1	CF_3–CF_2–CF_2–CF_2H	2.331
2	CH_3–CH_2–CF_2–CF_2H	0.904
3	CH_3–CH_2–CF_2–CF_3	3.150
4	CF_3–CF_2–CF_2–CF_2–CF_2–CF_2H	2.433
5	CH_3–CH_2–CF_2–CF_2–CF_2–CF_2H	1.087
6	CH_3–CH_2–CF_2–CF_2–CF_2–CF_3	3.467

group. One interesting point is that T_{max} of the γ relaxation is about 20 K higher in P4FM and P4FF (ω-monohydro fluoroalkyl samples) than in P5FM and P5FF (ω-trifluoro fluoroalkyl samples), respectively. This result suggests that the terminal –CF_2H causes an intermolecular interaction, perhaps through H–F interaction. It is of interest that the local molecular motion of side chains (the γ relaxation) is perturbed by an intermolecular interaction which is closely connected with the chemical structure.

When the dielectric relaxation behaviors between PFM (Figure 3) and PFF (Figure 4) are compared, the magnitudes of the γ relaxations are comparable to each other but the α relaxations are much larger in intensity for PFF than for PFM. These results seem to reflect the magnitude of the dipole moments in the polymer chains. The α-F substituent produces the large dipole moment on the backbone chains, and these polar backbone chains result in increasing the magnitude of the α relaxation, while the γ relaxation, due to the local molecular motion of alkyl side groups, is scarcely affected by the polarity of the α substituents. However, the γ relaxations in P4FM and P4FF (ω-monohydro fluoroalkyl samples) are somewhat larger in intensity than those in P5FM and P5FF (ω-trifluoro fluoroalkyl samples), respectively, which should impose a difference in the polarity between the terminal groups, –CF_2H and –CF_3. The dipole moments per one fluoroalkyl group for the γ relaxation (μ) was calculated by assuming the Onsager equation[16]

$$N\mu^2 = 3kT/4\pi(2\epsilon_0 + \epsilon_\infty)/3\epsilon_0[3/(\epsilon_\infty + 2)]^2(\epsilon_0 - \epsilon_\infty) \quad (2)$$

where ϵ_0, ϵ_∞, N, k, and T are the static dielectric constant, the high frequency limiting dielectric constant, the number of dipole moment per unit volume, the Boltzmann constant, and the absolute temperature, respectively. The values of ϵ_0 and ϵ_∞ were obtained from Cole–Cole plots which well obeyed the Cole–Cole equation.[17] The results obtained are listed in Table III, where β is the Cole–Cole distribution parameters of relaxation time and $\beta = 1$ means a single relaxation process. To evaluate how the polarity of the fluoroalkyl side group is responsible for the γ relaxation, we calculated the dipole moments of six fluoroalkanes, which can be considered as model compounds of the fluoroalkyl side groups, based on MNDO approximations.[18] The calculated results are listed in Table III, and the calculated configurations of compounds 1–3 are shown in Figure 7. The configurations of compounds 4–6 were similar to those of compounds 1–3, respectively. The configurations computed here should be those in the gaseous state at 0 K and so are considered to not express the configurations in the solid state. The calculated dipole moments (μ_{cal}) of the model compounds, therefore, are the values for the assumed computed ground state, which is fully populated only at 0 K. In the ω-monohydro fluoroalkyl samples (P4FM, P8FM, P4FF, and P8FF), the values fairly well coincide with the μ_{cal} values of the model compounds 2 and 4, but not with the μ_{cal} values of the model compounds 3 and 6 in the ω-trifluoro fluoroalkyl samples (for example, P5FM and P5FF). This result suggests that the configurations of the ω-trifluoro fluoroalkyl samples differ from those of the ω-monohydro fluoroalkyl samples. In fact, the large van der Waals radius of the F atom could twist the backbone chains in the solid state, as known in polytetrafluoroethylene.[19]

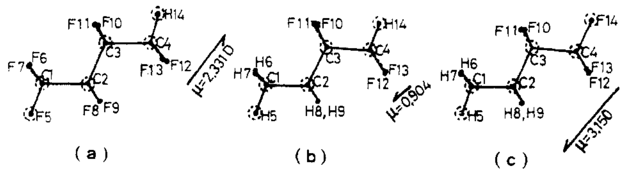

Figure 7. Configurations of three fluoroalkanes calculated by MNDO approximations: (a) compound 1, CF_3–CF_2–CF_2–CF_2H; (b) compound 2, CH_3–CH_2–CF_2–CF_2H; (c) compound 3, CH_3–CH_2–CF_2–CF_3.

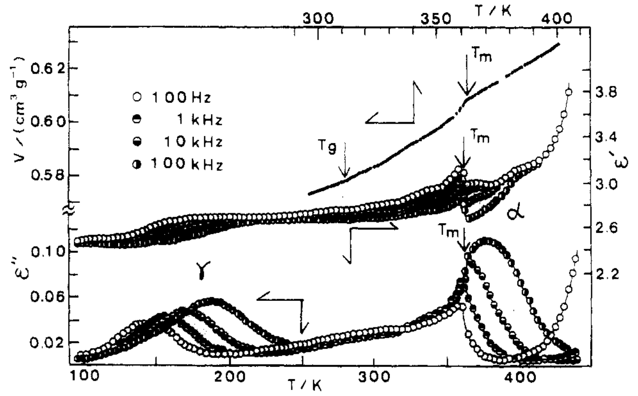

Figure 8. Temperature dependences of dielectric constant (ϵ') dielectric loss (ϵ'') and specific volume (V) for P17FM.

Figure 8 shows the temperature dependence of the dielectric constant (ϵ') and the loss (ϵ'') for P17FM at several frequencies. Apparently, both ϵ'–temperature and ϵ''–temperature curves show an abrupt change near 360 K besides the α and γ relaxations, which suggests an existence of a phase transition. This phase transition may be due to a melting of crystalline region of P17FM, since the phase transition temperature is well consistent with the melting points (T_m) of P17FA (acrylate polymer) and P17FM which were obtained as 358 K by Okawara et al.[4] and 360 K by us,[20] respectively, from DSC measurements. The melting phenomenon of P17FM is also observed in the thermal expansion data for P17FM, as shown in Figure 8. The abrupt change in specific volume (V) is also seen near 360 K, and the glass transition appears near 310 K. The thermal expansion coefficients were estimated as 5.4 × 10^{-4} below T_g and 7.1 × 10^{-4} above T_g and 8.6 × 10^{-4} K^{-1} above T_m, respectively. The melting behavior of the crystalline region was not observed for the other samples in the present dielectric data. The formation and structure of the crystallites in PFM and poly(ω-trifluoro fluoroalkyl acrylate)s (PFA) have been reported by a few researchers.[3,4]

In the crystalline region, the fluoroalkyl side chains were packed into a layer structure whose thickness was nearly equal to the length of the fluoroalkyl chain. Moreover, the spacing between the fluoroalkyl chains in the layer was about 4.92 Å, which is almost the same as that of polytetrafluoroethylene crystallites. Such crystallizations of fluoroalkyl side groups occurred only for the longer fluoroalkyl groups, for example, when $n \geq 7$ for both PFM and PFA homologues of $-COO-CH_2-(CF_2)_n-CF_2H$ esters[3] and when $m \geq 6$ for PFA homologues of $-COO-CH_2-(CF_2)_m-CF_3$ esters[4], and their T_{max} values increased proportional to n with increasing n. The α relaxation seems to be depressed by the existence of the crystallites below T_m and abruptly appears above T_m. Therefore the fluoroalkyl groups are considered to be in an liquid state above T_m which causes the α relaxation. X-ray diffraction studies are in progress for PFM and PFF homologues in our laboratories to clarify the structure of crystallites.

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