

Dielectric and Dynamic Mechanical Behaviour of Poly(vinyl chloride) Containing Small Amounts of Cholesterol, Cholesteryl Chloride, and Cholesteryl Benzoate

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(Received December 3, 1982)

ABSTRACT: Poly(vinyl chloride) (PVC) containing small amounts of cholesterol (Ch), cholesteryl chloride (ChCl), and cholesteryl benzoate (ChBz) were studied by dielectric and dynamic mechanical spectrometry. Dielectric data were fitted to the WLF equation. Using the C_1 , C_2 constants obtained for pure PVC, PVC+additive systems fitted well the WLF curve by an appropriate choice of reference temperature, T_0 . T_0 of PVC+additives were lower than that of pure PVC. α - and β -peaks in PVC+additives occurred at temperatures lower than those in pure PVC. β -Peak intensities in DMA spectra decreased on adding Ch and ChBz. This may be ascribed to the possible specific interactions of C-Cl dipoles in PVC with OH from Ch or aromatic protons from ChBz. Such a suppression of β -peak is described as antiplasticization by earlier workers. The behaviour of these additives with PVC differed from that with poly(vinyl acetate) or poly(butyl methacrylate) due to differences in apparent enthalpy of activation (ΔH_a) for the α -process.

KEY WORDS Dielectric Behaviour / Poly(vinyl chloride) Systems / Cholesteryl Compounds / Dynamic Mechanical Analysis /

In our earlier studies¹⁻³ we reported the dielectric behaviour of poly(vinyl acetate) (PVAc) and poly(*n*-butyl methacrylate) (PBMA) containing small concentrations of cholesteryl liquid crystalline compounds. The shift of the α -relaxation peak in these polymers to high temperatures and low frequency has been attributed to the antiplasticizing effect of cholesteryl compounds. In this paper, we report on the dielectric and dynamic mechanical behaviour of poly(vinyl chloride) (PVC) containing small amounts of cholesterol, cholesteryl chloride and cholesteryl benzoate.

In PVAc and PBMA, the dipoles are located in flexible groups pendant to the main chain. In contrast, the C-Cl dipole in PVC is rigidly attached to the main chain. Further, the three additives used here are crystalline compounds at room temperature, with the crystal→isotropic liquid transition temperature higher than the glass transition temperature of PVC.

EXPERIMENTAL

Materials

A suspension polymerized PVC and having a viscosity average molecular weight of 85,000 was washed with methanol to remove any soluble impurities and additives. It was further washed with hot benzene to remove low molecular weight fractions and dried *in vacuo*. Commercial grade lead silicate (1.75 phr) and lead stearate (0.25 phr) were used as a stabilizer and lubricant respectively (phr=parts per hundred parts of resin). Cholesterol, cholesteryl chloride, and cholesteryl benzoate (Aldrich Chemical Co. UK) were used as delivered.

Preparation of Films

Thin films (about 0.2 mm thick) were solution cast by dissolving PVC and an appropriate amount of the additive in tetrahydrofuran. In all cases, transparent films were obtained, indicating the compatibility of additives at these concentrations with

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PVC. These compositions were therefore used for compression moulding of films as follows: a mixture of PVC powder, stabilizer, lubricant and the cholesterol additive (2–7 phr) was hot blended at 130°C for 10 min, roll-milled at 165°C for 7 min, and then compression moulded into sheets of 20 × 20 × 0.05 cm dimensions. All samples were annealed at 60°C for one week. Samples were cut in 63 mm diameter discs for dielectric studies and in 10 × 19 mm strips for dynamic mechanical measurements.

Dielectric Measurements

Dielectric measurements were carried out on a Schering bridge of Rohde and Schwarz at 10 frequencies in the range 0.5 to 200 kHz. At each frequency, the measurements were conducted in the range from 55°C to 130°C covering only the α -relaxation region of PVC.

Specimens were clamped between polished stainless steel electrodes of guarded electrode cell assembly. The holder assembly was immersed in a thermostated oil bath whose temperature could be controlled to within $\pm 0.05^\circ\text{C}$. Two thermocouples were embedded in the electrode for monitoring the sample temperature, and the thermo-e.m.f. was read on a digital microvoltmeter. The cell was maintained for 30 min at the desired temperature before taking the readings. Capacitance and $\tan \delta$ were measured at the set temperature for all required frequencies. Following completion of the measurements, sample thickness was measured at room temperature. From the thickness and calibrated values of the air capacitance of the cell, ϵ' and ϵ'' were calculated.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements were made on a Du Pont DMA-981 instrument. For storage modulus measurements, the samples were clamped in the vertical mode. To improve the sensitivity, the samples were mounted in the horizontal mode for damping measurements; in this case, however, the absolute storage modulus could not be evaluated. Measurements were made in the temperature range from -120 to $+110^\circ\text{C}$ at a heating rate of 5°C min^{-1} and a 2.5 l min^{-1} flow rate of N_2 . The amplitude of oscillations used was 0.2 mm peak to peak. The plots on an X-Y-Y' recorder gave the resonant frequency (f , Hz) of the sample and damping (V , mV) versus temperature of the sample. The

instrument was calibrated using standard samples of poly(methyl methacrylate) and poly(carbonate) supplied by the manufacturer. From the recorder plots, at very closely spaced points, E' and $\tan \delta$ were calculated as follows:

$$E' = \frac{(4\pi^2 f^2 J - K)}{2W \left(\frac{L}{2} + D \right)^2} \left(\frac{L}{T} \right)^3 \times \left[1 + 0.71 \left(\frac{2T}{L} \right)^2 - 0.1 \left(\frac{2T}{L} \right)^3 \right] \quad (1)$$

$$\tan \delta = C \cdot V / f^2 \quad (2)$$

$$E'' = E' \cdot \tan \delta \quad (3)$$

where J is the moment of inertia of the system; K , the pivot spring constant; L , T , and W , the sample length, thickness and width (m); D , the clamping distance (m); and C , the damping constant. Values of $(\tan \delta)_{\text{max}}$ are given in Table I.

RESULTS

Dielectric loss versus temperature data at few selected frequencies are given in Figures 1–3. From the data of $\tan \delta$ versus temperature at each frequency (f) constants a , b , and c in eq 4 were evaluated by regression analysis:

$$\ln \tan \delta = \ln \tan \delta_m + a(T - T_m) + b(T - T_m)^2 + c(T - T_m)^3 \quad (4)$$

where T_m is the temperature at which the $\tan \delta$ - T curve shows a maximum. Data for f_m and T_m were used to obtain f_m at a reference temperature T_0 of the Williams-Landel-Ferry (WLF) equation⁴

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (5)$$

where a_T is the shift factor and C_1 and C_2 are constants related to the free volume. The plot of shift factor $\log a_T$ versus $(T - T_0)$ is shown in Figure 4. The dotted line corresponds to the WLF equation with the universal WLF constants $C_1 = 8.86$, $C_2 = 101.6$; the solid line corresponds to the fitting of our experimental data on pure PVC for which the constants obtained are $C_1 = 4.72$, $C_2 = 61.83$ by setting $T_0 = T_g + 50 = 400 \text{ K}$. With these values of C_1 and C_2 for systems PVC + cholesterol, PVC + cholesterol chloride, and PVC + cholesterol ben-

zoate, T_0 at each concentration were evaluated for the best fit of the data by regression analysis.

From the WLF equation, the apparent enthalpy of activation ΔH_a is obtained as

$$\Delta H_a = 2.303 R \cdot C_1 \cdot C_2 T^2 / [C_2 + (T - T_0)]^2 \quad (6)$$

Since ΔH_a rapidly decreases with temperature in the region $T > T_0$, for the sake of comparison of ΔH_a for different systems, we have given ΔH_a at $(T_0 - 25)^0$ in Table I.

Table I gives the glass transition temperatures T_g for these systems measured on a thermomechanical analyser (TMA) at a heating rate of 8°C min^{-1} . By setting $T_m = 0$ eq 4 can be used for regression

analysis of the data ε' versus temperature to obtain ε_0 and ε_∞ . The dielectric strength, $\Delta\varepsilon'$, is defined as $\varepsilon_0 - \varepsilon_\infty$. Together with these values and the measured area of the curve $\tan \delta$ versus $(1/T)$, the enthalpy of activation was calculated from the relation⁵:

$$\Delta H_a = \frac{\pi R \cdot \varepsilon'}{2(\varepsilon_0 \cdot \varepsilon_\infty)^{1/2}} \int \tan \delta d(1/T) \quad (7)$$

ΔH_a calculated from eq 7 agreed well with that given in Table I and are not given here.

The temperature maximum for α - and β - relaxation peaks in the DMA measurements were read

Table I. Dielectric and dynamic mechanical behaviour of PVC + additive systems

	$T_g/^\circ\text{C}$ (from TMA)	Dielectric (at 1 kHz)		$(T_0 - 50)$ $^\circ\text{C}$	ΔH_a at $(T_0 - 25)^\circ\text{C}$ kJ mol^{-1}	DMA		DMA ($\tan \delta$) _m	
		$T_m/^\circ\text{C}$	$(\tan \delta)_m$			$T_\alpha/^\circ\text{C}$	$T_\beta/^\circ\text{C}$	(α)	(β)
Pure PVC	77.0	102.3	0.1255	77	579.5	95	-10	1.2	0.02880
PVC + Cholesterol	3 phr 78.0	91.6	0.1723	63	537.1	91.4	-23	1.41	0.0180
	5 phr 76.1	90.25	0.1434	61	531.2	90.0	-24	1.65	0.01663
	7 phr 74.2	89.55	0.1147	58	522.3	91.2	-26	1.85	0.0153
PVC + Cholesteryl benzoate	2 phr 79.0	94.25	0.1396	70	558.1	91.0	-15.2	1.15	0.0145
	4 phr 77.2	93.25	0.1135	67	549.0	89.17	-18.00	1.2	0.0140
	6 phr 76.5	92.45	0.1529	64	540.0	87.0	-21.8	1.05	0.0125
PVC + Cholesteryl chloride	2 phr 69.0	92.1	0.1550	62	538.5	89.6	-16.5	1.8	0.0390
	4 phr 64.0	90.0	0.1480	60	532.5	87.1	-21.9	1.85	0.03625
	6 phr 61.0	86.45	0.1490	57	523.6	85.0	-31.3	1.96	0.02850

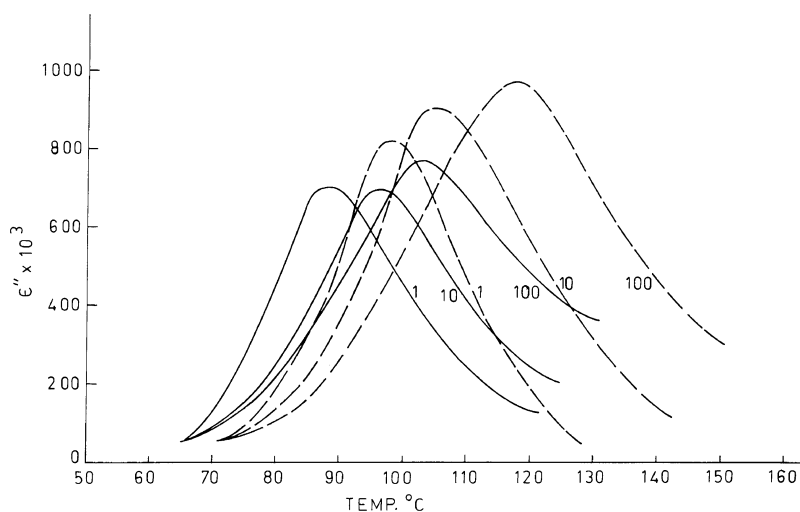


Figure 1. Dielectric loss versus temperature plots for pure PVC (dotted line curves) and PVC + (7 phr) cholesterol (solid line curves) at 1 kHz, 10 kHz, and 100 kHz.

from the direct $X-Y-Y'$ recorder plots and are given in Table I as T_{α} and T_{β} temperatures.

Plots of storage modulus E' and $\tan \delta$ vs. temperature are given in Figures 5—7.

DISCUSSION

From the results in Table I, it is evident that glass transition temperatures T_g for polymer+Ch (2

phr)/ChBz (2 phr) are slightly higher than T_g of pure PVC. For other concentrations and for PVC+ChCl, however, these values are lower than T_g of pure PVC. T_{α} temperatures obtained from DMA measurements for all systems are higher than corresponding T_g by about 10—15°C. Such differences have been reported earlier⁶ for other systems. T_{α} for PVC+additive systems are lower than T_{α} for pure PVC. It may also be noted that the values of

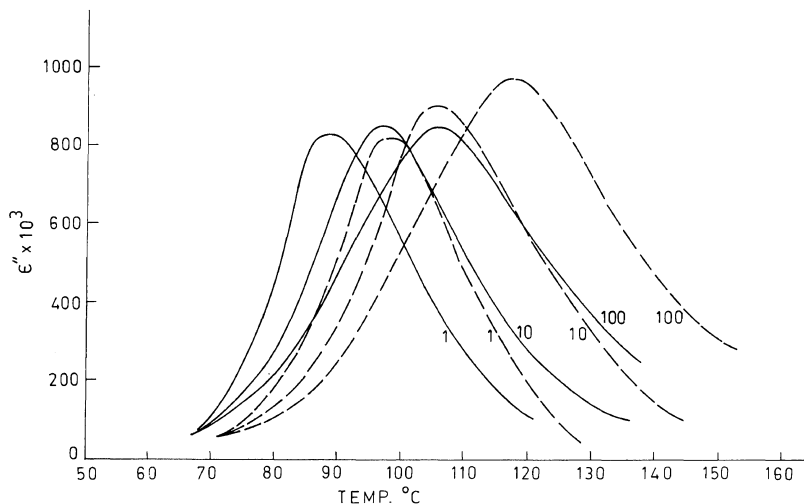


Figure 2. Dielectric loss versus temperature plots for pure PVC (dotted line curves) and PVC+(6 phr) cholesteryl benzoate (solid line curves) at 1 kHz, 10 kHz, and 100 kHz.

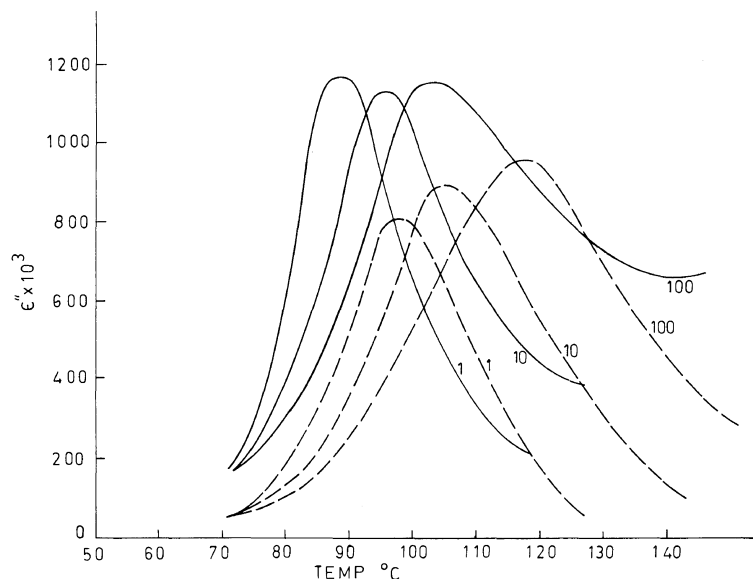


Figure 3. Dielectric loss versus temperature plots for pure PVC (dotted line curves) and PVC+(6 phr) cholesteryl chloride (solid line curves) at 1 kHz, 10 kHz, and 100 kHz.

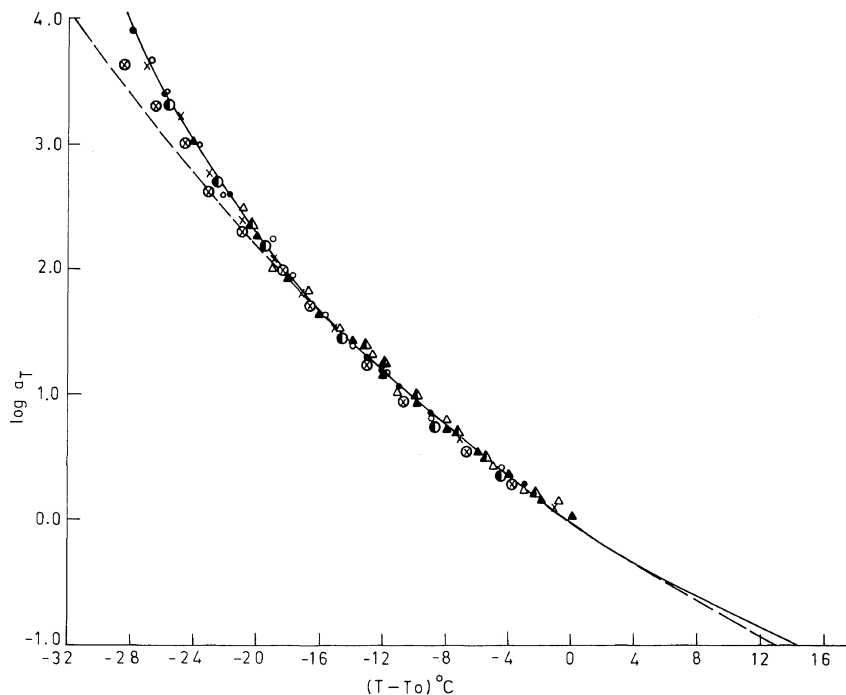


Figure 4. WLF universal curve (dotted line) and WLF curve fitted for pure PVC (solid line) experimental points for PVC+additives, cholesterol (Δ , 3; \blacktriangle , 5; \blacktriangleleft , 7 phr) cholesteryl chloride (\otimes , 4 \times 6 phr) and cholesteryl benzoate (\bullet , 2; \bullet , 4; \circ , 6 phr).

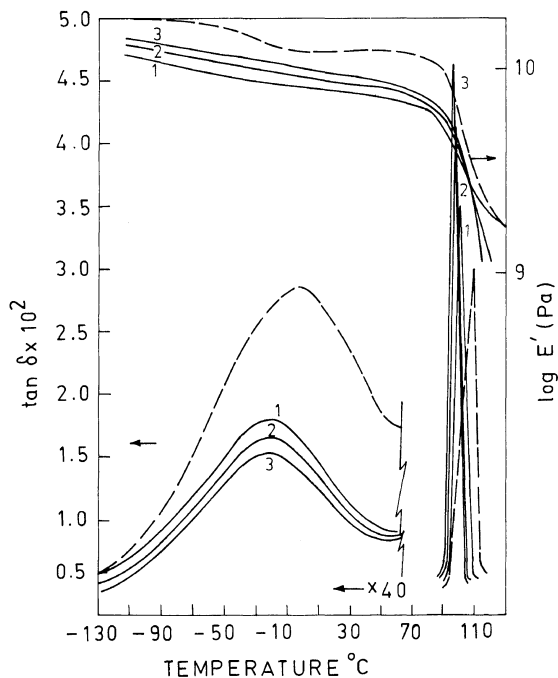


Figure 5. DMA plots for E' and $\tan \delta$ versus temperature for pure PVC (dotted line curve) and PVC+cholesterol (solid line curves) 1, 3 phr; 2, 5 phr; 3, 7 phr.

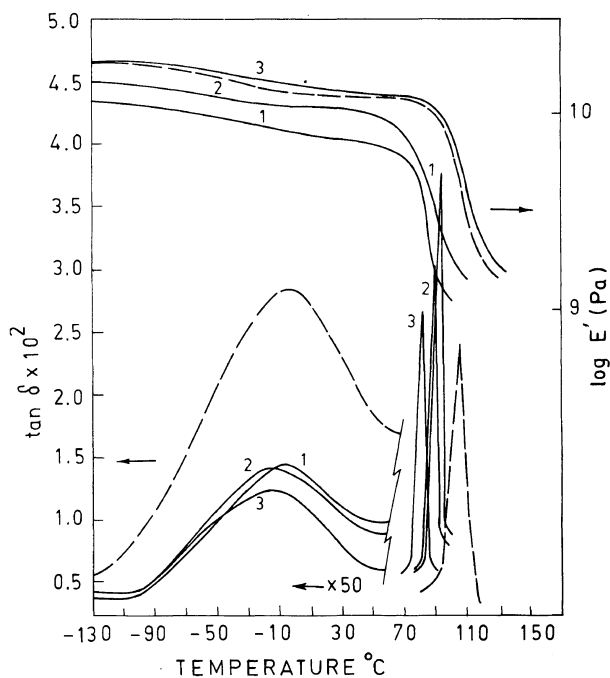


Figure 6. DMA plots for E' and $\tan \delta$ versus temperature for pure PVC (dotted line curve) and PVC+cholesteryl benzoate (solid line curves) 1, 2 phr; 2, 4 phr; 3, 6 phr.

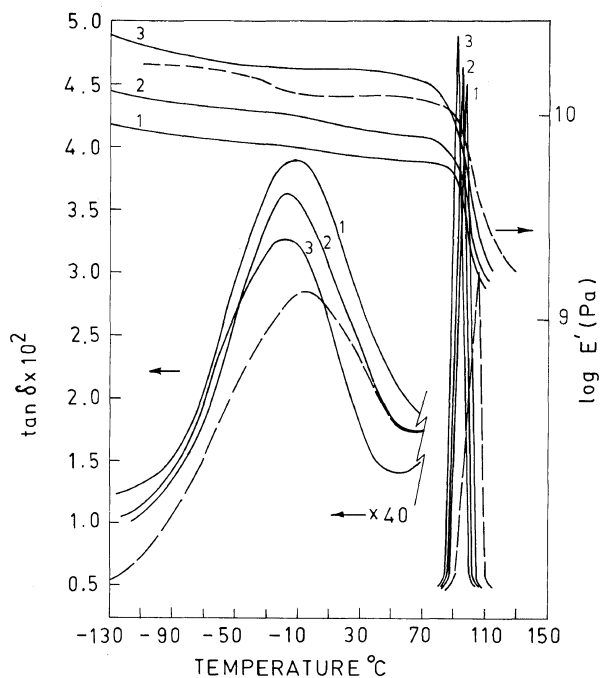


Figure 7. DMA plots for E and $\tan \delta$ versus temperature for pure PVC (dotted line curve) and PVC+cholesteryl chloride (solid line curves) 1, 2 phr; 2, 4 phr; 3, 6 phr.

($T_0 - 50$) for all systems are very close to T_g of the system under consideration because of $T_0 = (T_g + 50)$ in the WLF relationship. From Figures 1–3 and 5–7, it can be seen that all loss curves have shifted to low temperatures by the addition of cholesterol, cholesteryl chloride and cholesteryl benzoate. Both the dielectric and DMA measurements show that the shift to low temperatures and the broadening increase with increasing concentration of additives. Thus, the addition of small molecules—though highly crystalline in nature—to PVC has an overall effect of increasing segmental mobility. We could not use higher concentrations of these additives owing to their limited solubilities in PVC. The intensities of the α -peaks in both the dielectric loss (ϵ'') and DMA $\tan \delta$ curves for PVC + additive systems are higher than that in pure PVC and decrease with increasing amount of additive.

For pure PVC, the β -relaxation occurs at about -10°C and is very weak in intensity. For this reason, DMA measurements were conducted with samples mounted in the horizontal mode. T_β temperatures shift to low temperatures with increasing additive concentration. The β -peaks for PVC + cholesterol and PVC + cholesteryl benzoate have much lesser intensities than those in pure PVC (see Figures 5, 6). Such a decrease in intensity of a β -peak or virtual suppression of the peak in some cases has been regarded as an antiplasticization effect.^{7,8} It has been argued⁹ that the additives which normally act as plasticizers for PVC behave as antiplasticizers when used in very small amounts ($< 10\%$). In the present systems *viz.* PVC + cholesterol and PVC + cholesteryl benzoate, a specific interaction between the C–Cl dipole of PVC and the OH group from cholesterol or the aromatic protons from cholesteryl benzoate is possible, and this may be responsible for the lowering of the β -peak intensity. This situation did not occur in the PVC + cholesteryl chloride systems. In the three systems, the storage modulus in the glassy region is less than that in pure PVC and increases with increasing additive concentration.

Thus, dielectric and DMA measurements indicated the plasticizing effect of crystalline additives—cholesterol, cholesteryl benzoate, and cholesteryl chloride. These observations are not in line with those on systems consisting of PVAc and PBMA with the same additives and in which antiplasticization was observed. The main difference in these systems arises from rigid C–Cl dipoles attached to the main chain in the case of PVC, while the ester group dipoles in PVAc and PBMA are in the pendant group and are much more flexible. Thus, the activation energy for the α -relaxation in PVC is much higher ($\approx 448 \text{ kJ mol}^{-1}$) than that in either PVAc¹ ($\approx 272 \text{ kJ mol}^{-1}$) or in PBMA² ($\approx 123 \text{ kJ mol}^{-1}$). Hence, an additive molecule which can easily hinder the segmental motion in PVAc or PBMA would not be able to do so in the case of PVC unless there is a very strong specific interaction between the additive and the monomeric units of PVC.

Acknowledgement. We are thankful to the Department of Atomic Energy (Government of India) for providing financial support for this work.

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