Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Dielectric and Viscoelastic Behavior of Poly-(*n*-Butyl Methacrylate) Containing Cholesteric Compounds

Dinkar D. Deshpande[a]; Chandana Basu[a]; Madhav V. Pandya[a]
[a] Department of Chemistry, Indian Institute of Technology, Bombay, India

To cite this Article Deshpande, Dinkar D. , Basu, Chandana and Pandya, Madhav V.(1988) 'Dielectric and Viscoelastic Behavior of Poly-(*n*-Butyl Methacrylate) Containing Cholesteric Compounds', Journal of Macromolecular Science, Part A, 25: 9, 1071 — 1087

To link to this Article: DOI: 10.1080/00222338808053408

URL: http://dx.doi.org/10.1080/00222338808053408

J. MACROMOL. SCI.–CHEM., A25(9), pp. 1071-1087 (1988)

DIELECTRIC AND VISCOELASTIC BEHAVIOR OF POLY-(*n*-BUTYL METHACRYLATE) CONTAINING CHOLESTERIC COMPOUNDS

DINKAR D. DESHPANDE,* CHANDANA BASU, and
MADHAV V. PANDYA

Department of Chemistry
Indian Institute of Technology, Bombay
Powai, Bombay 400076, India

ABSTRACT

Dielectric and dynamic mechanical behavior of poly(*n*-butyl methacrylate) (PBMA) containing small concentrations of cholesteryl chloride (ChCl), cholesteryl caprylate (ChCp), and cholesteryl laurate (ChL) have been studied in the temperature range -20 to 80°C. Tan $\delta_{\max}$ (dielectric and mechanical) in all systems containing an additive shifts to lower temperature compared to that in pure PBMA. In the glassy region, the dynamic storage modulus E' for all the PBMA plus additive systems is higher than that for pure PBMA. This behavior is similar to the β-peak suppression and the increase in tensile strength of poly(vinyl chloride) on addition of a small concentration of plasticizer. Using the WLF equation with C_1 and C_2 obtained from the data on pure PBMA, the reference temperature T_0 for PBMA plus additive systems are determined for the best fit of the experimental points to the WLF curve and are in agreement with measured glass-transition temperatures. With respect to T_0 of pure PBMA, the T_0 of PBMA plus additive systems are lowered, and the lowering due to these additives is in the order ChL < ChCp < ChCl. From spectrophotometric studies

---

*To whom correspondence should be addressed.

in solutions of polymer plus additives, equilibrium constants for the 1:1 and 1:2 complexes between the polymer and the additive are evaluated. The magnitude of the equilibrium constant K_1 increases in the order ChL > ChCp > ChCl, and hence it is concluded that the extent of β-peak suppression depends on the strength of polymer-additive interaction.

INTRODUCTION

The transitions observed in thermomechanical spectra (especially α- and β-transitions) of polymers are sensitive to interaction with neighbors and to changes in the free volume [1-3]. Thus, addition of any foreign substance of low molecular weight gives rise to changes in relaxation or relaxation temperatures, intensity of the loss peak, and changes in T_g. Many additives lower the T_g due to reduced interchain interaction and increased free volume. However, some additives are found to hinder sterically the segmental motion and show an altogether different behavior. Sometimes these additives increase the glass transition temperature; sometimes, without increasing T_g, they suppress the β-relaxation and hence increase the tensile modulus. Though such additives are described as antiplasticizers, as yet no satisfactory mechanism of antiplasticization explains all the observations.

In earlier publications from this laboratory [4-6], several cholesteric liquid-crystalline materials were found to be antiplasticizers for PVAc, PVC, and PBMA. Cholesteric liquid-crystalline compounds are thermotropic liquid crystals with molecular weights higher than 400. They have nuclei that are polarizable, planar, and rigid. They maintain local parallel or nearly parallel arrangement of the long axis of molecules over macroscopic distances. The structure of the parent compound is given in Fig. 1. The hindrance to the segmental motion caused by these additive may be due to different factors, e.g., 1) liquid-crystalline nature of the additive, 2) geometry of the additive, and 3) the specific dipolar interaction between the additive and the polymer chain. The liquid-crystalline nature of the additive does not play any role as there is no direct correlation between the shift and the liquid-crystalline transition temperature. Density measurements have not given any conclusive evidence for close packing due to occupation of voids in polymer by the additive [4] and hence the results cannot be explained solely on the basis of a free-volume model [3]. In the present work, therefore, a detailed study has been undertaken to understand the mechanism of antiplasticization by dielectric, dynamic mechanical, spectroscopic, and viscometric studies of poly(n-butyl methacryl-

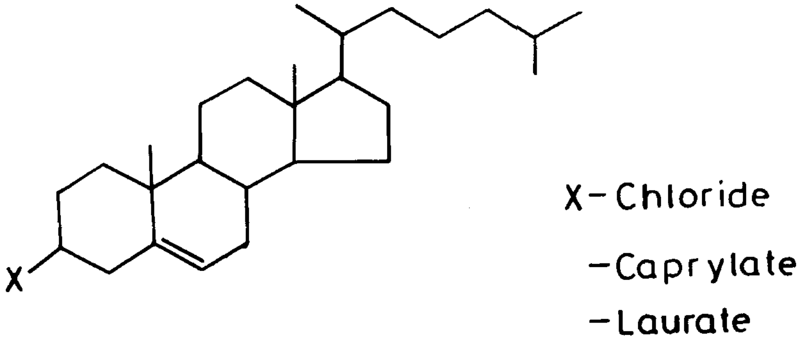

FIG. 1. Structure of the cholesteryl additive.

ate) (PBMA) containing cholesteryl chloride (ChCl), cholesteryl caprylate (ChCp), or cholesteryl laurate (ChL).

EXPERIMENTAL

Poly(*n*-Butyl Methacrylate)

Poly(*n*-butyl methacrylate) used for the present studies was synthesized by free-radical polymerization of *n*-butyl methacrylate in toluene at 70°C with benzoyl peroxide as initiator. The number-average molecular weight of PBMA was 120 000.

Films for dielectric, dynamic mechanical, and thermomechanical studies were prepared by a solution casting technique. The polymer was weighed with the required amount of cholesteryl additive, and a homogeneous solution of this mixture was prepared. The solvent was allowed to evaporate slowly. The films were kept in a vacuum oven for 7 days at room temperature. After the preliminary drying, the films were kept in a vacuum oven for another 7 days at 50°C to remove the last traces of solvent. For each additive, films with three different concentrations, from 1 to 6 wt%, were prepared and used without further analysis for composition. Higher concentrations of the additives could not be used due to limitation of miscibility.

Dielectric Measurement

Capacitance and tan δ were measured on a Rohde-Schwartz (West Germany) dielectric test bridge (VK 3520) using a three-electrode (guarded) cell immersed in a thermostatic bath. It is a Scherring-type bridge with manual null balancing at each frequency to obtain the capacitance and dissipation factor in the frequency range from 30 Hz to 300 kHz. The signal generator frequencies were calibrated with a standard frequency counter.

Dynamic Mechanical Analysis

Dynamic mechanical analysis was carried out on a Du Pont Model DMA-981 instrument in the range from -15 to 75°C. The instrument monitors the resonance frequency of the sample and damping as a function of temperature, and these parameters are plotted on a X-Y-Y′ recorder of the Du Pont 990 thermal analyzer. The storage modulus (E') and tan δ are then calculated by the equations

$$E' = [(4\pi^2 f^2 J) - K]\,(L/T)^3/2W(L/2 + D), \qquad (1)$$

$$\tan\delta = (CV/f^2) \qquad (2)$$

where E' is the modulus, f is the oscillation frequency, J is the moment of inertia, K is the pivot spring constant, L is the sample length, T is the sample thickness, W is the sample width, D is the clamping distance, C is the damping constant, and V is the measured damping voltage.

Viscometry

A fixed amount of solute containing different ratios of polymer and the other component was dissolved in 10 mL of toluene, and the time of flow of the solution was measured at 30°C with an Ubbelohde viscometer. The reduced viscosity of a solution is given by

$$\eta_{\text{red}} = \left(\frac{t_1}{t_0} - 1\right)/c = \eta_{sp}/c, \qquad (3)$$

where t_1 and t_0 are the efflux time of the solution and the solvent, respectively, and c is the concentration of polymer in solution in g/dL. Plots of the change in the reduced viscosity versus weight fraction of additive are indicative of the interaction between the two components [7-10].

UV-Visible Spectrophotometry

UV-visible spectra were recorded on a Shimadzu UV-visible spectrophotometer. Near equimolar quantities of polymer and additive were measured first to obtain the molar extinction coefficient of the complex and the equilibrium constant for 1:1 complex formation reaction. Then higher concentrations of cholesteryl additive were measured to find the second equilibrium constant. All the measurements were carried out in a carbon tetrachloride solution at 25°C.

Thermomechanical Analysis

The present TMA system was fabricated from indigenously available components mainly for the purpose of monitoring T_g and for creep studies. The model is similar to the Stanton-Redcroft instrument. Two separate mini-furnaces were fabricated, one for use from ambient temperature to 400°C, and another for use from -150 to 150°C. The scan rate for all the samples studied was 8°C/min, obtained with a temperature programmer. The sample size was 10 g.

Differential Scanning Calorimetry

Differential scanning calorimetry studies of two samples, PBMA and PBMA + 6 phr ChCl, were made with a Perkin-Elmer DSC-2B instrument.

RESULTS

PBMA and PBMA systems containing different amounts of cholesteryl chloride (ChCl), cholesteryl caprylate (ChCp) and cholesteryl laurate (ChL) were investigated by both the dielectric bridge method and the dynamic mechanical analyzer.

Dielectric Data and Treatment of Data

The relaxation processes of PBMA and PBMA plus additive were studied by the dielectric method at seven different frequencies from 25 to 80°C. Dielectric loss (tan δ) data points at each frequency were fitted to a polynomial of the type

$$\ln X = B_0 + B_1(T - T_m) + B_2(T - T_m)^2 + B_3(T - T_m)^3 + B_4(T - T)^4, \quad (4)$$

where T_m is the temperature at which the tan δ versus temperature curve shows a maximum. The value of T_m was chosen so that the difference between the calculated and the experimental value of tan δ was less than 2%.

A typical tan δ versus temperature plot is shown in Fig. 2. The temperature, T_m, at the maximum tan δ thus obtained was used to construct Arrhenius plots (Figs. 3-5) which were used to determine the apparent activation energies. However, the plots are slightly curved, and therefore the data were fitted to the WLF equation

$$a_T = \log f_0/f = C_1(T - T_0)/[C_2 + (T - T_0)], \quad (5)$$

where C_1 and C_2 are the WLF constants, f and T are the experimental data points (i.e., f and T_{max} of the tan δ versus temperature plots), T_0 is the WLF

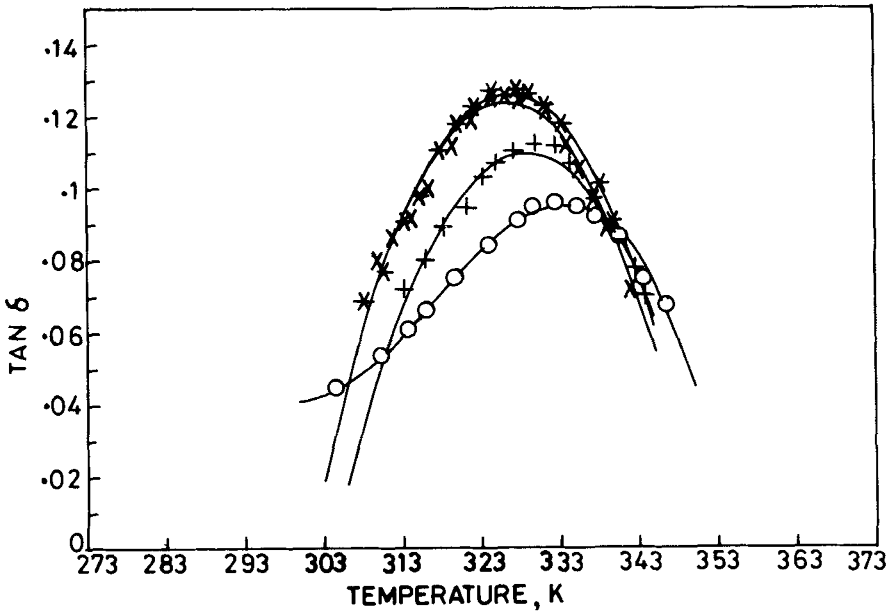

FIG. 2. Dielectric tan δ vs temperature plots for PBMA plus ChCl system at 1 kHz frequency: 0% ChCl (○), 2% ChCl (+), 4% ChCl (X), 6% ChCl (*).

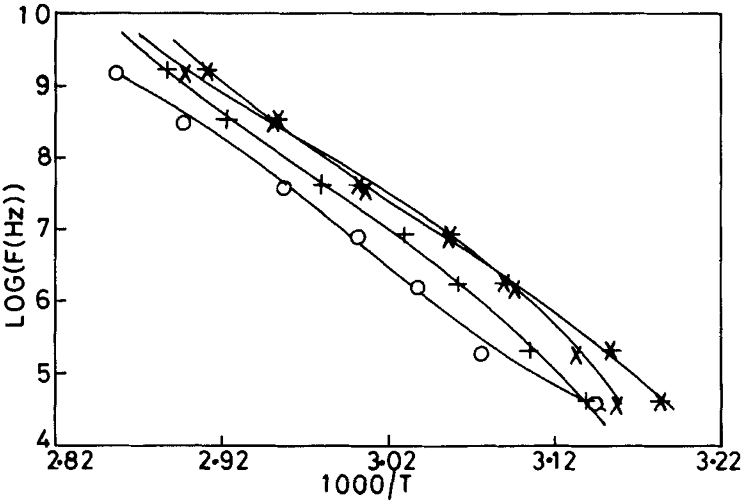

FIG. 3. Dielectric Arrhenius plots (log f vs $1/T_{max}$): PBMA plus ChCl system. Notation as in Fig. 1. Points experimental, lines fitted.

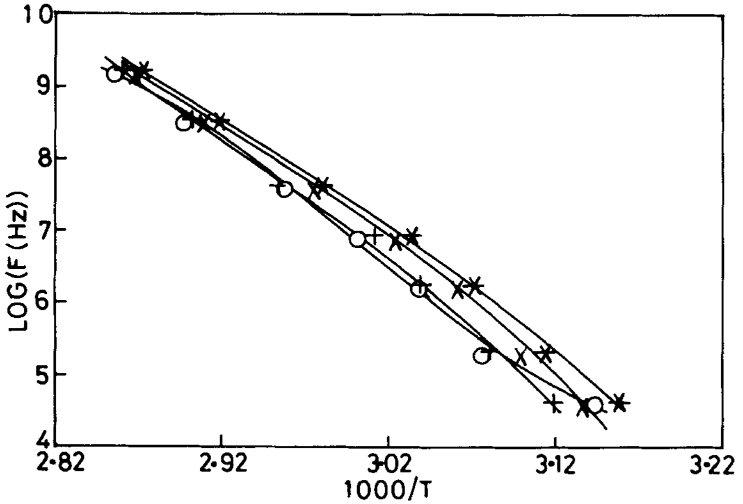

FIG. 4. Dielectric Arrhenius plots (log f vs $1/T_{max}$): PBMA plus ChCp system, 0% ChCp (○), 1% ChCp (+), 2% ChCp (X), 3% ChCp (*). Points experimental, lines fitted.

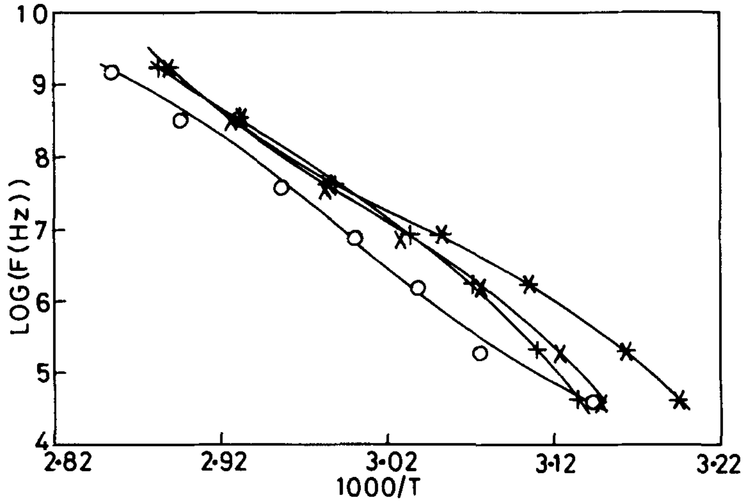

FIG. 5. Dielectric Arrhenius plots (log f vs $1/T_{max}$): PBMA plus ChL system, 0% ChL (○), 2% ChL (+), 3% ChL (X), 4% ChL (*). Points experimental, lines fitted.

reference temperature, and f_0, corresponding to T_0, was obtained from the fitted log f versus $1/T_{max}$ plot. First, C_1 and C_2 were obtained as follows from the data for pure PBMA, taking $T_0 = T_g + 50$: f_0 was taken from the log f versus $1/T_{max}$ plot corresponding to T_0. Then from f_0 and T_0, the shift factors, a_T, can be calculated, and the equation

$$(T - T_0)/\log(a_T) = -[(T - T_0)/C_1 + C_2/C_1] \qquad (6)$$

solved for C_1 and C_2. The constants thus obtained for PBMA are $C_1 = 6.3106$ and $C_2 = 108.84$.

It may be assumed that the WLF constants have the same values for the PBMA plus additive systems as for pure PBMA and that only the reference temperature T_0 would differ for each system. Using the WLF constants C_1 and C_2, T_0 was estimated for the other systems to obtain the best fit of the experimental data. The solid line of Fig. 6 is the WLF curve for pure PBMA, while the points are for PBMA and PBMA plus different concentrations of additive. The T_0 value of each system is given in Table 1 for comparison.

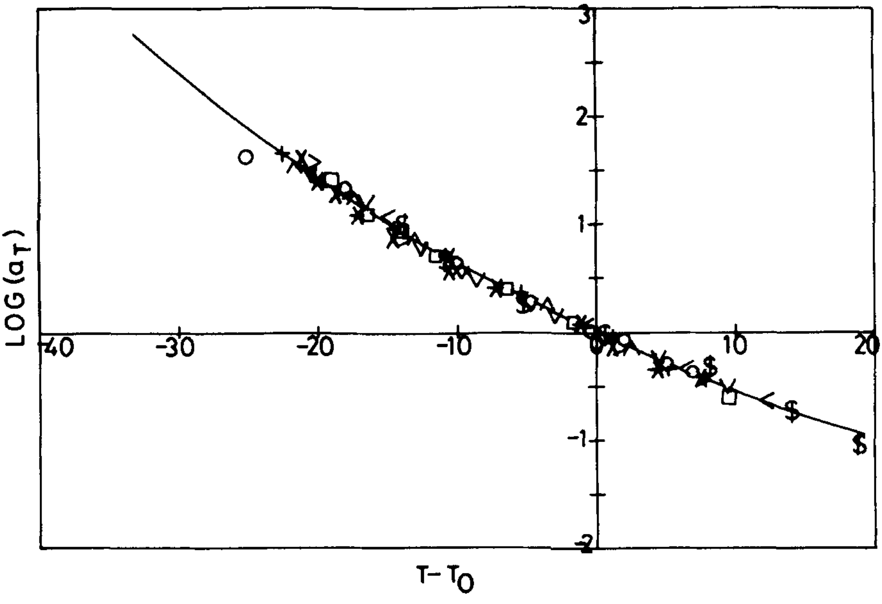

FIG. 6. WLF curve. PBMA plus cholesteryl additive systems: PBMA (○); 2% ChCl (+), 4% ChCl (X), 6% ChCl (*); 1% ChCp (∧), 2% ChCp (∨), 3% ChCp (<); 2% ChL (>), 3% ChL (◉), 4% ChL ($).

Dynamic Mechanical Analysis

The dynamic mechanical analysis was carried out in the vertical mode of clamping. The samples' resonant frequency and damping are digitally displayed on the front panel and also continuously plotted on the X-Y-Y′ recorder as a function of sample temperature. The raw plots were further used to calculate tan δ and the storage modulus, E', at closely spaced temperatures (see Figs. 7-9).

Studies of the Interaction between PBMA and Cholesteryl Liquid Crystalline Additives by Viscometry

Viscosity coefficients of systems containing two solutes can be written in the form

TABLE 1. Dielectric and Dynamic-Mechanical Measurements on PBMA Plus Additive Systems

System	Additive concentration, phr	Dielectric		TMA	DSC	Dynamic mechanical analysis		
		T_0, (WLF), K	T_g, (T_0 - 50), K	T_g, K	T_g, K	$T_{\alpha B}$	Tan $\delta_{max} \times 10^2$ [a]	E' at 300 K, GPa
PBMA	–	343	293	291	293.6	343	7.35 (6.8)	4.93
PBMA + ChCl	2	341	291	290	–	337	4.02 (6.5)	5.85
	4	337.5	287.5	288	–	337	4.61 (6.5)	6.99
	6	334	284	285	285	333	5.29 (6.5)	10.14
PBMA + ChCp	1	342	292	291	–	339	4.69 (6.7)	6.16
	2	339	289	289	–	337	6.01 (6.7)	7.95
	3	336	286	285	–	335	4.79 (6.7)	7.29
PBMA + ChL	2	339	289	289	–	331	4.08 (6.8)	6.53
	3	336.5	286.5	286	–	333	6.74 (7.1)	5.95
	4	327	277	278	–	329	4.44 (6.5)	5.85

[a] The frequency (in Hz) at which tan δ is maximum is given in parentheses.

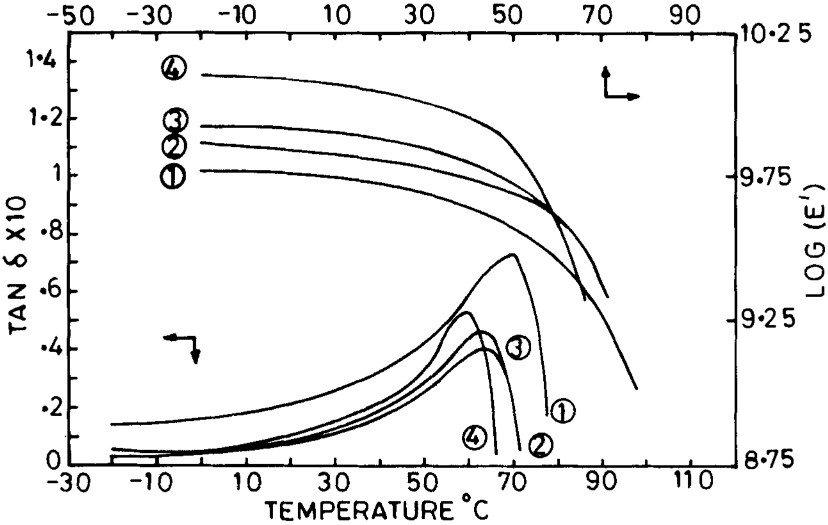

FIG. 7. DMA log E' and tan δ vs temperature plots for PBMA plus ChCl system: 0% ChCl (1), 2% ChCl (2), 4% ChCl (3), 6% ChCl (4).

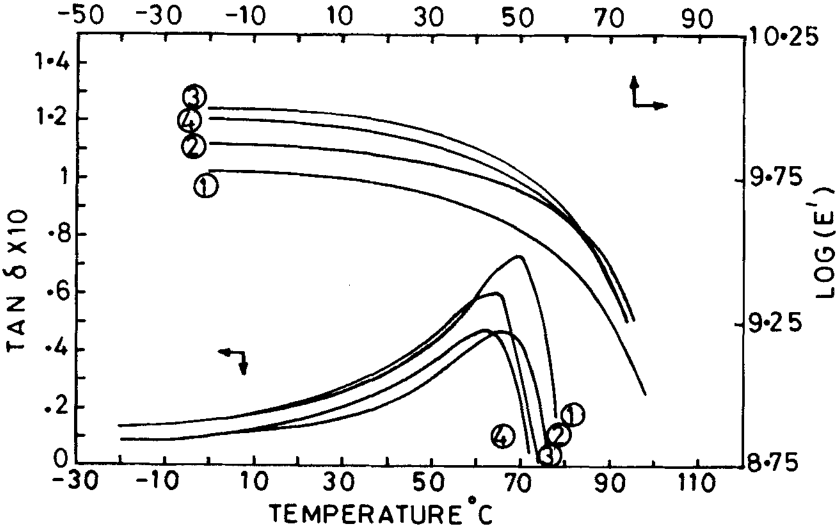

FIG. 8. DMA log E' and tan δ vs temperature plots for PBMA plus ChCp system: 0% ChCp (1), 1% ChCp (2), 2% ChCp (3), 3% ChCp (4).

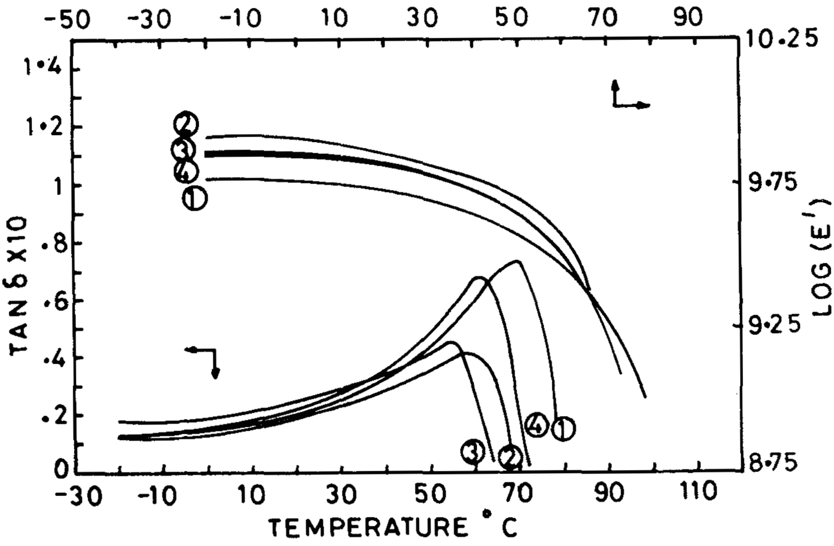

FIG. 9. DMA log E' and tan δ vs temperature plots for PBMA plus ChL systems: 0% ChL (1), 2% ChL (2), 3% ChL (3), 4% ChL (4).

$$\eta_{\text{mix}} = w_1\eta_1 + w_2\eta_2 + \Delta\eta, \tag{7}$$

where w_1 and w_2 are weight fractions of Components 1 and 2, respectively, and η_1 and η_2 are the viscosity coefficients of the pure components in the same solvent with viscosity coefficient η_0, while $\Delta\eta$ represents the nonideality of mixing. Dividing Eq. (7) by η_0 and C, and rearranging leads to

$$\Delta\eta_{\text{red}} = \Delta\eta/(\eta_0 C) = (1/C)\,[(\eta_{\text{mix}})_{sp} - w_1(\eta_1)_{sp} - w_2(\eta_2)_{sp}], \tag{8}$$

where C is the total solute concentration.

A minimum in the plot $\Delta\eta_{\text{red}}$ versus weight fraction of component indicates that there is association between the components [7-10]. Challa et al. [11, 12] studied association between isotactic and syndiotactic PMMA in various solvents. Complex formation studies of monomer (MMA) and cholesteryl additives has been reported [13, 14]. Plots according to Eq. (8) are given in Fig. 10. The minima in the plots indicate that there is interaction between PBMA and the additives.

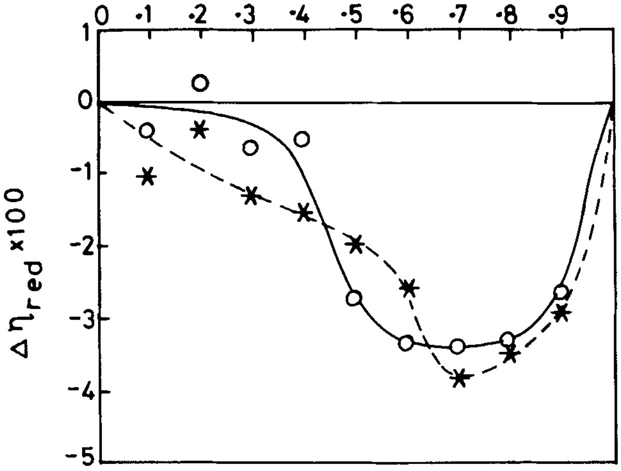

FIG. 10. Change in reduced viscosity $\Delta\eta_{red}$ vs weight fraction of cholesteryl compound, PBMA plus ChCl (○), PBMA plus ChL (*).

Complex Formation Studies

The general equation for the equilibria involved in complex formation between polymer and additive is here given by

$$\mathrm{P} + n\mathrm{A} = \mathrm{PA}_n.$$

If the equilibria occur stepwise, the equilibrium constant for the first step will be given by

$$K_1 = [\mathrm{PA}_1] / \left\{ \mathrm{P}_0 - [\mathrm{PA}_1]\, [\mathrm{A}_0 - (\mathrm{PA})] \right\}, \tag{9}$$

where P_0 and A_0 are the initial concentrations of polymer and additive. By taking equimolar quantity of additive and polymer, it can be assumed that one polymer chain is interacting with only one molecule of additive. For 1:1 complex formation, the general equation proposed by Rose and Drago [15] is

$$(K_1)^{-1} = \frac{A - \epsilon_p \mathrm{P}_0 - \epsilon_a \mathrm{A}_0}{(\epsilon_c - \epsilon_p - \epsilon_a)} - \mathrm{P}_0 - \mathrm{A}_0 + \mathrm{P}_0 \mathrm{A}_0 \frac{(\epsilon_c - \epsilon_p - \epsilon_a)}{A - \epsilon_p \mathrm{P}_0 - \epsilon_a \mathrm{A}_0}, \tag{10}$$

where P_0 and A_0 are initial concentrations of polymer and additive, ϵ_p, ϵ_a, and ϵ_c are molar extinction coefficient of polymer, additive, and complex, respectively, and A is the absorbance of the solution. The equilibrium concentration of the 1:1 complex, $[PA_1]$, can be obtained from Eq. (9) as

$$[PA_1] = K_1 [A] P_0/(1 + K_1 [A]), \tag{11}$$

where [A] is the equilibrium concentration of A. For the second molecule of cholesteryl compound interacting with the polymer chain,

$$K_2 = [PA_2]/[PA_1][A],$$

and hence,

$$[PA_2] = K_1 K_2 [A]^2 P_0/(1 + K_1 [A]). \tag{12}$$

The total absorbance in this case is given by

$$\begin{aligned} A_{\text{total}} &= A_{\text{complex}} + A_{\text{polymer}} + A_{\text{additive}} \\ &= \epsilon_c [\{K_1 [A] P_0/1 + K_1 [A]\} + \{K_1 K_2 [A]^2 P_0/1 + K_1 [A]\}] \\ &\quad + \epsilon_p [P_0 - K_1 [A] P_0/1 + K_1 [A]] + \epsilon_a [A] \end{aligned} \tag{13}$$

The molar extinction coefficient of complex and the equilibrium constant for 1:1 complex formation can be determined by using the intersection method to solve Eq. (10) when near equimolar quantities of polymer and additives are used.

K_1, ϵ_c, ϵ_p, and ϵ_a being known, and with a trial value of K_2, Eq. (13) is solved for the equilibrium concentration of additive [A] by the Newton-Ramphons method. These parameters (K_1, $[PA_1]$, and $[PA_2]$) are used to calculate the absorbance of solution at a different wavelength. K_2 is varied, and the entire calculation is iterated until good agreement is obtained with the experimental absorbance at another wavelength. The K_1 and K_2 values so obtained are given in Table 2.

Thermomechanical Analysis

Glass-transition temperatures, T_g, obtained from TMA studies are reported in Table 1.

TABLE 2. Complexing Equilibrium Constants from Spectrophotometry

System	$K_1 \times 10^{-5}$, L/mol	K_2, L/mol
1. PBMA + ChCl	0.238	640
2. PBMA + ChCp	5.7	355
3. PBMA + ChL	24.31	70

Differential Scanning Calorimetry

The glass-transition temperatures of two samples, PBMA and PBMA plus 6 phr ChCl, were measured by DSC, and the T_g's thus obtained are reported in Table 1.

DISCUSSION

The dielectric data can be well represented by the WLF equation (Fig. 6) when the constants C_1 and C_2 are obtained by fitting the data on pure PBMA and using the reference temperature T_0 as $T_g + 50$. The same constants are used to represent the data on PBMA plus additive systems by varying T_0 to obtain the best fit. For PBMA plus additive systems the dielectric glass transition is then obtained as $T_0 - 50$. As seen from Table 1, these values compare very well with those measured by TMA or by DSC. In all cases it will be noticed that the glass transition in PBMA plus additive systems is lower than that of pure PBMA.

The temperatures at which the loss tangent from the DMA results is maximum is given in Table 1 as the DMA glass transitions. These are higher than the values obtained from dielectric measurements or TMA. It is known [16] that DMA glass transitions are usually higher than those measured by the static method. The trends of the variations in PBMA plus additive systems are the same as those for dielectric behavior. In all cases the intensities of the loss peaks for PBMA plus additive systems are less than that for pure PBMA, and the concentration dependence of the intensity is not uniform. For all the PBMA plus additives systems, the storage modulus E' is higher than that of pure PBMA in the glassy region. With increasing concentration of additive, however, E' is found to vary differently in each case.

It has been reported that many cholesteryl liquid-crystalline additives shift the dielectric α-relaxation peak in PVAc to higher temperature [6], while the

α-relaxation temperature in PVC is lowered and the β-peak is suppressed [5]. For PBMA [4], some cholesteryl compounds do shift the α-relaxation to higher temperature, but cholesteryl oleyl carbonate shifts it to a lower temperature.

It may be pointed out that the pendent group in PBMA has a sizable length and, hence, the relaxation is a combined α,β-process, i.e., the segmental motion is coupled with side-group motion. The dielectric results on the α,β-relaxation process should, therefore, be analyzed in the light of the DMA results.

An additive molecule may hinder the side-group motion or the segmental motion in the polymer chain by interaction with repeat units, attaching loosely to the active sites on the chain or by entering in the voids of the polymer matrix. In such a case the α-relaxation shifts to higher temperature, provided the strength of the interaction is sufficient to increase the energy of activation for the process. If the interaction is weak, only the β-process can be affected. Thus, PVC plus cholesteryl additives show only suppression of the β-process while PVAc plus cholesteryl additives show that the α-relaxation shifts to higher temperature.

In the light of this, the effect of additives on the α,β-relaxation process of PBMA can be explained as follows. All the additives to PBMA used in this work shift the dielectric as well as DMA loss peaks to lower temperature and the intensity of the loss peaks is lowered (Figs. 7-9). The most important observation is that the storage modulus E' is higher in PBMA plus additive systems compared to E' of pure PBMA in the glassy region. Such an increase in tensile strength is indicative of suppression of the β-process, a phenomenon described as antiplasticization.

The lowering of the dielectric or DMA glass-transition temperature in PBMA plus additive systems varies in the order ChL < ChCp < ChCl. The changes in reduced viscosities given in Fig. 10 suggest that specific interaction between polymer and cholesteryl compound is possible due to the observed minimum in each plot.

The equilibrium constants for complex formation between the polymer and the cholesteryl compound were, therefore, determined by spectrophotometric studies (Table 2). As expected, $K_2 \ll K_1$, and higher-order equilibrium constants can be neglected without affecting the accuracy of the evaluation and, especially, without affecting the main conclusions.

Table 2 reveals that variation of K_1 is in line with the observed variation in T_g. This supports the idea that the specific interaction of polymer and cholesteryl compound is responsible for the suppression of the β-process in PBMA. The order of variation in K_1 is ChL > ChCp > ChCl, indicating that the association between PBMA and ChL is stronger than that between PBMA and ChCp or ChCl. K_2 values for the same systems, however, show an opposite trend. A possible reason is that ChL, being larger in size, the second-step equilibrium is difficult to establish as the second ChL molecule would have difficulty in approaching the same chain. On the other hand, ChCl being smaller in size and more polar, a second molecule of ChCl can easily attach itself to another active site of the same polymer chain. In other words, the enthalpy of interaction would overcome the entropy contribution to make the free energy more negative, causing K_2 to be higher.

In conclusion, the dielectric and dynamic mechanical behavior of PBMA plus cholesteryl compounds is governed by the extent of interaction between the two components.

REFERENCES

[1] R. F. Boyer, *Polymeric Materials,* American Society for Metals, 1973, Chap. 6.
[2] R. F. Boyer, *Rubber Chem. Technol., 36,* 1303 (1968); *J. Polym. Sci., Part C, 14,* 267 (1966).
[3] M. G. Wyzgoski and G. S. Yeh, *Polym. J., 4,* 29 (1973).
[4] D. D. Deshpande and N. R. Kandaswamy, *Polymer, 22,* 1211 (1981).
[5] D. D. Deshpande and V. K. Tiwari, *Polym. J., 15,* 377 (1983).
[6] D. D. Deshpande, N. R. Kandaswamy, and V. K. Tiwari, *J. Appl. Polym. Sci., 30,* 2869 (1985).
[7] Y. Tanaka, Hitotsujuzagi, Y. Shimura, A. Okada, H. Sakuraba, and Y. Sakata, *Makromol. Chem., 177,* 3055 (1976).
[8] E. M. Barall and J. F. Johnson, *J. Macromol. Sci.–Rev. Macromol. Chem., C17,* 137 (1979).
[9] D. D. Deshpande and A. V. Rao, *Polym. Bull., 2,* 485 (1980).
[10] D. D. Deshpande and A. V. Rao, *Polymer, 21,* 548 (1980).
[11] G. Challa, A. De Boer, and Y. Y. Tan, *Int. J. Polym. Mater., 4,* 439 (1976).
[12] A. De Boer and G. Challa, *Polymer, 17,* 633 (1976).
[13] A. V. Rao, PhD Thesis, I.I.T. Bombay, 1980.
[14] P. Aravindakshan, PhD Thesis, I.I.T. Bombay, 1983.
[15] N. J. Rose and R. S. Drago, *J. Am. Chem. Soc., 81,* 6138 (1959).
[16] V. K. Tiwari, PhD Thesis, I.I.T. Bombay, 1983.

Received May 26, 1987
Revision received January 4, 1988