Colloid Polym Sci 273:524–532 (1995)

ORIGINAL CONTRIBUTION

A.A. Mansour

Dielectric method for detection of phase separation and its kinetics in TMPC/PS blends

Received: 18 March 1994
Accepted: 3 January 1995

Dr. A.A. Mansour (✉)
Chemistry Department
Faculty of Science
Cairo University
Orman-Gzia, Egypt

Abstract A new method for the detection of phase separation and its kinetics through real-time measurements is presented using the dielectric technique. The kinetics of phase separation were determined for a blend of tetramethyl bisphenol-A polycarbonate TMPC and polystyrene PS at different temperatures. The temperature dependence of the rate constant of phase separation was determined. The activation energy of phase separation process is found to be equal to 46 kcal/mole. In addition, it was possible to determine the variation in the composition of the TMPC-rich phase with time. The results obtained were compared with the literature data and were found to be in good agreement.

Key words Blends – tetramethyl polycarbonate – polystyrene – LCST – phase separation – kinetics

Introduction

Although phase behavior of polymer blends has received much attention in the last few years [1–10], the available experimental data in the literature and the methods of detection of phase separation and its kinetics are very limited and still under refinement and development. For this reason, the present work aims at developing a new method for the detection of phase separation and its kinetics in the early stages using the dielectric technique. This would enrich the experimental basis and therefore supports the theoretical approach of this complex subject.

The phase behavior was studied mainly by three methods, namely, determination of the cloud point [9], light scattering [8] and differential scanning calorimetry [1, 4, 9]. On the other hand, the effect of phase separation on the distribution of relaxation times of the glass process at temperatures above and below LCST for two composition ratios of PS/PoCS was studied dielectrically by Alexandrovich et al. [10]. However, there is no experimental data obtained from dynamical methods such as mechanical or dielectric spectroscopy concerning the kinetics (rate constant and activation energy) of phase separation monitored by real time measurements. In the frame of the present work, an example of polymer blends which has a low critical solution temperature (LCST) behavior is used. The blend of polystyrene, PS, and tetramethylbisphenol-A polycarbonate, TMPC, is used as there are available literature data about its phase behavior [1–9]. The miscibility of PS and TMPC was first reported by Shaw [1], who suggested low critical solution temperature behavior for this blend. Casper and Morbitzer [2] constructed a complete phase diagram for PS/TMPC blend according to their DSC measurements. The onset temperature for phase separation estimated for PS/TMPC with composition ratio of 40/60 was found to be about 240 °C [2]. In addition, there is available information about the physical properties of this blend concerning the density [3, 9] thermal analysis [4, 7, 9] mechanical [3] and neutron scattering [8, 11, 12]. Regarding the dielectric measurements, Nagi et al. [13] reported about the dielectric measurements of this blend over a narrow range of frequency between 10^3–10^5 Hz. For this reason, a dielectric relaxation spectra of pure TMPC and TMPC/PS blend over a wide frequency range of 10^{-2}–10^{-5} Hz at different temperatures ranging from 130° to 220 °C are also presented.

Experimental

Tetramethyl bisphenol-A polycarbonate TMPC was kindly supplied from Bayer, (Leverkusen, FRG) under the technical name MPC100-KLI-1141. It has a molecular weight of 40000 g/mole. Polystyrene PS was kindly supplied from BASF (Ludwigshafen, FRG) under the commercial name PS-168N 003 glasklar and which has a molecular weight of 250 000 g/mole.

TMPC/PS blends were prepared by dissolving the corresponding weights of polymers in methylene chloride. Methylene chloride is recommended to avoid crystallization of the blend [7]. The solution of the blend was then poured on a polyethylene sheet and left to dry in air for 3 days. Thereafter, the films were dried in a vacuum oven at 60 °C for 24 h then at 190 °C for 4–6 h. About 0.1 gram blend was then taken and pressed between two thin copper electrodes at the same temperature. The pure polymers were pressed directly without dissolution. The capacitance of the condensers used was about 30 pF.

The calorimetric glass transition temperatures were determined for a series of blends with different TMPC contents, namely, 0, 25, 50, 75, and 100% wt using a Perkin–Elmer DSC-7 in the section of Calorimetry, University of Ulm, FRG.

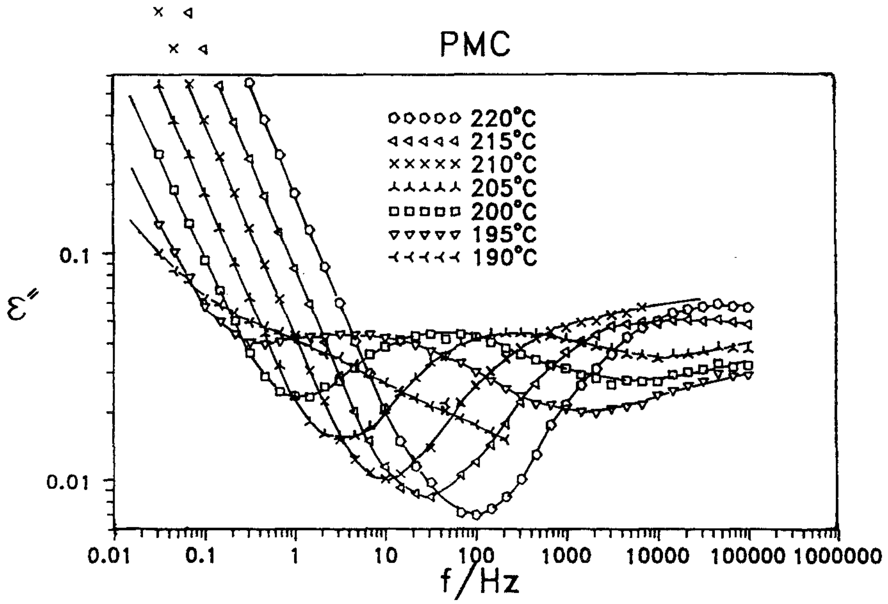
The dielectric properties were measured for pure polymers and 50:50 TMPC/PS blend in the frequency and temperature range 10^{-2}–10^5 Hz and 130°–220 °C, respectively.

Two units were used for the dielectric measurements, one for the frequency scan measurements, and the other for the time-scan runs. The frequency scan measurements were carried out using an Impedance/Gain-Phase Analyzer SI-1260 from Schlumberger. The circuit of the bridge will be published later on. The accuracy of this bridge is 10^{-3} for $\tan \delta$. The measuring cell is very similar to that used before [14]. The second dielectric bridge is a PL-DETA instrument supplied by Polymer Laboratories, England. The frequency range of the PL-DETA bridge is 10^2–10^5 Hz. This equipment was employed in the time-scan measurements. After each time-scan measurement the sample was annealed for 2–3 h at 190 °C in order to obtain a single-phase blend before carrying out the measurements at the next temperature.

Results and discussions

The variation of the dielectric loss parameter with frequency of pure TMPC is plotted on a double logarithmic scale and is presented in Fig. 1. Two relaxation processes (glass and local) and a low frequency conductivity contribution can be observed in this figure. The ionic conductivity process is characterized by the rapid decrease in the

Fig. 1 Dielectric loss of pure TMPC with a logarithmic scale over the frequency at different temperatures



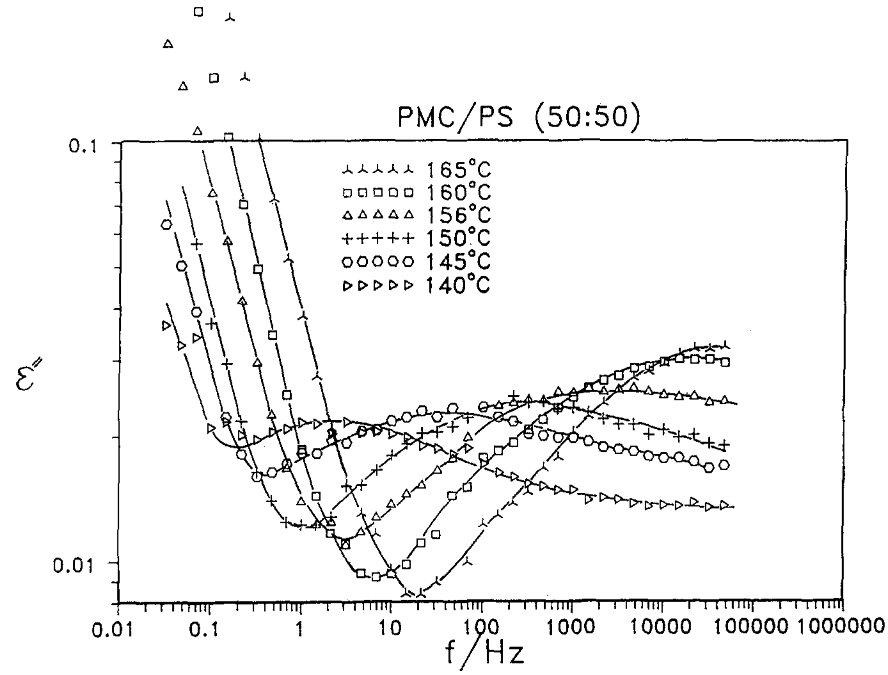


Fig. 2 Dielectric loss curves of 50:50 TMPC/PS blend at various temperatures

dielectric loss with increase of the frequency. The glass process is due to the microbrownian cooperative reorientation of the polymeric segments and appears at frequencies higher than those of the ionic conductivity. At the high frequency tail of the glass process, the local relaxation process is exhibited. This process is attributed to limited reorientation of some loosely packed segments and appears in the majority of polymers [15].

Similar observations are found in Fig. 2 which represents the measurements of 50:50 TMPC/PS blend. A comparison between Fig. 1 and Fig. 2 shows that the height of the blend is lower than that of the pure TMPC by about 50%. This finding can be attributed to the fact that the observed glass relaxation process of the blend is mainly due to the dipolar reorientation of TMPC segments. This suggestion can be supported by the calculation of the relaxation strength $\Delta\varepsilon$ using the dielectric loss curves in Fig. 1 and applying the Kramers–Kronig equation [16] which reads:

$$\Delta\varepsilon = \frac{2}{\pi} \ln 10 \int_{-\infty}^{\infty} \varepsilon'' d(\log f)\,. \tag{1}$$

The value of $\Delta\varepsilon$ obtained for the glass process of TMPC equals 0.3 and it is about 10 times greater than that of pure PS, which equals 0.036 [17]. On the other hand, it can be also seen that the width of the glass process in the blend is greater than that of pure TMPC (taking into account the difference in the drawing scale between Figs. 1 and 2). This finding is similar to that observed before [12, 18] and also in the case of oligostyrene/polystyrene blends with concentrations higher than 10% wt oligomer [17]. This result can be attributed to the concentration fluctuation which will lead to a great variation in the dynamical constraints of segments as a result of blending with PS [19]. However, analysis of the spectrum using an empirical relaxation function to study the effect of blending on the distribution of relaxation times will be done and reported later.

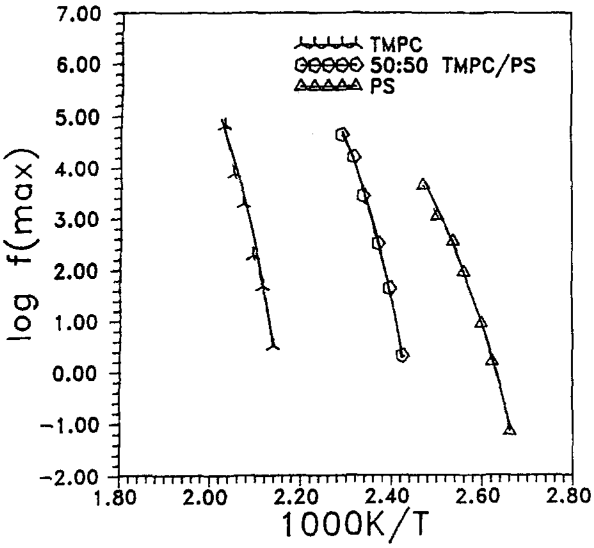
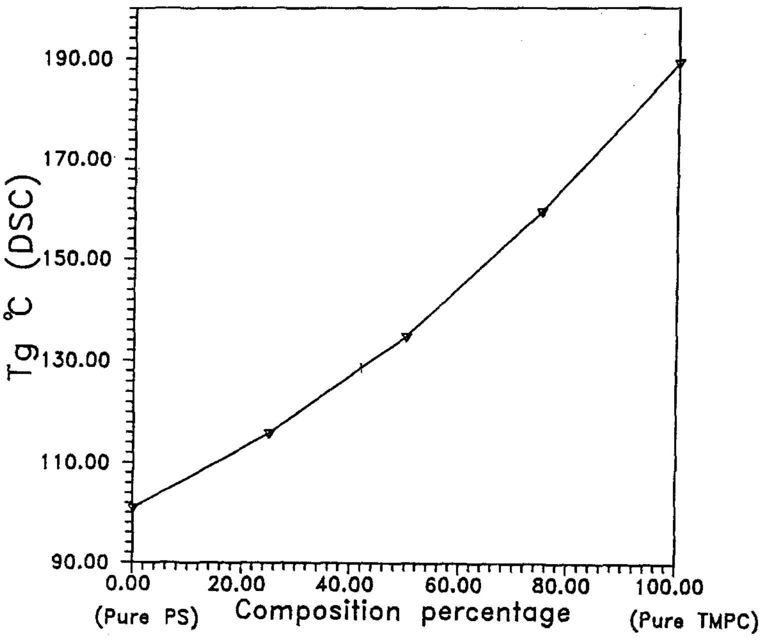


Fig. 3 Activation diagram of the glass processes of pure polymers and the 50:50 TMPC/PS blend

Figure 3 is the activation energy diagram for pure TMPC, PS and the 50:50 TMPC/PS blend. It is clear that

Fig. 4 Variation of the calorimetric glass transition temperature with the composition of the blend



the activation curve of the blend lies between those of the pure polymers. This result implies that the TMPC and PS are compatible on a segmental level and form one phase, whose dynamics is represented by only one glass relaxation process. This is also evidenced by the calorimetric measurements, which shows that the blends prepared have only one glass transition temperature. Moreover, the glass temperature varies systematically with changing the composition of the blends, as can be seen in Fig. 4.

Kinetic measurements

Theoretically, the kinetics of phase separation could be detected dielectrically by following the variation in the relaxation frequency, f_m, of the common glass process of the blend by time at a certain temperature. However, direct measurements of both of the dielectric glass process and the time are not possible for several reasons, mainly:

1) The spinodal decomposition takes place within a few minutes, so that it would be impossible to detect this phenomenon using frequency scan measurements, as the shortest time required for a proper frequency scan measurement is not less than 10 min.
2) The critical temperature, at which the phase separation occurs is quite high, so that the relaxation frequency of the glass process of the one-phase blend is out of the normally available frequency range ($> 10^8$ Hz at 240 °C), as can be seen in Fig. 3.

These two problems can be solved in a way similar to that suggested by Illers et al. [4] for their calorimetric measurements procedure. This can be done by a rapid quenching of different samples after annealing for different time intervals at a certain temperature. The samples obtained can be measured dielectrically to determine the dielectric glass transition temperature [17] at different annealing time by a similar method to that described before [4]. However, this procedure is time consuming since the samples quenched at different time intervals must be thoroughly measured dielectrically to obtain a proper activation diagram, which will be then used in the determination of *Tg* for each sample [17]. At the same time, this quenching method cannot be considered as a real time measurement of the kinetics of phase separation. Moreover, several conditions must be satisfied to allow successful measurements which are very similar to that listed by Illers et al. [4]:

1) The equilibrium state at temperature *T* can be frozen by quenching.
2) *Tg*'s of the one-phase homogeneous mixtures can be determined and vary monotonically with composition.
3) *Tg*'s of the pure components are sufficiently far from one another.

It is now clear that one of the main difficulties of the detection of the kinetics of phase separation is to achieve a fast frequency scan measurement. Therefore, it was interesting to try to make a fast frequency scan measurement in a limited frequency range of 10^2–10^4 Hz (to save time) at temperatures in the range of the LCST. This fast measurement is facilitated by the powerful temperature-controlling system of the PL-DETA equipment together with the low

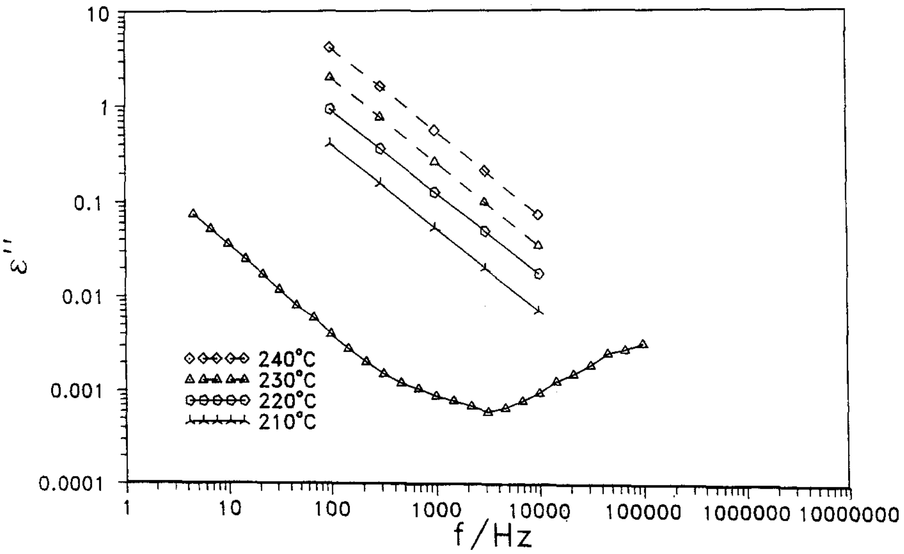


Fig. 5 Frequency dependence of the dielectric loss obtained by direct measurements (solid lines) and by extrapolation (dashed lines); see text

mass of the sample (0.1 gram) . The sample was heated at a rate of 40 °C/min from 150 °C to $T - 10$ °C then with 5 °C/min, where T is the temperature of measurements. This was done to avoid overheating of the sample. The measurement was started directly as the temperature sensor read the required temperature. After finishing the measurements at a certain temperature, the sample temperature was reduced slowly to 190 °C and annealed for 2 h to again obtain a single-phase blend before the next temperature was measured by the same sequence. The same was also done in the case of time-scan measurements. The results obtained for the temperatures 210° and 220 °C are presented in Fig. 5. Unfortunately, for temperatures higher than 220 °C, it was not possible to measure fast enough before total phase separation, so that the slope of ionic conductivity process was greater than the unity. For this reason, the sample was annealed at 230 °C for about 30 min to attain equilibrium, then the frequency scan measurement was carried out. The results obtained show that the loss values are lower than that obtained for the temperatures 210° and 220 °C, and also lower than that expected for 230 °C (the dashed lines are obtained from extrapolation, as shown below), as can be seen in Fig. 5. It must be stated here that the same finding is also observed for the temperatures 210° and 220 °C. This finding means that as the phase separation process is activated, the dielectric loss value (ionic conductivity) at a given frequency decreases.

This phenomenon could be understood as follows:

As the phase separation process is activated two phases will start to form, one phase is rich in PS, while the other is rich in TMPC. The glass transition of the former phase will decrease while that of the latter will increase. The extent of change in the glass transition temperature of both phases is proportional to the degree of phase separation [4]. As a consequence of the increase in the glass transition temperature of the TMPC rich phase, the ionic conductivity will be strongly restricted (and therefore the dielectric loss values will decrease) as a result of the formation of bulky domains with higher viscosities which will then restrict the ionic mobility.

Accordingly, one can make use of this phenomenon to detect the kinetics of phase separation through real-time measurements by following the variation of the dielectric loss values with time at a certain temperature.

However, the following conditions must be satisfied in order to achieve successful kinetic measurements:

1) The measurement of the dielectric loss is fast enough to supply precise real-time measurements. This can be done by measuring the dielectric loss at only one selected frequency.
2) The frequency of the measurements must be chosen in a region at which there is no overlap between the ionic conductivity and the glass process. In addition, the dielectric loss value at this chosen frequency must have values lying in the accuracy range of the equipment at the measuring temperature.

It can be seen in Fig. 2 that the ionic conductivity process is low and well separated from the glass process. On the other hand, the PL-DETA can satisfy the second condition. In order to choose the frequency of measurements, the loss values and the position of the ionic conductivity process must be known for the one-phase blend at the temperature range of the phase separation

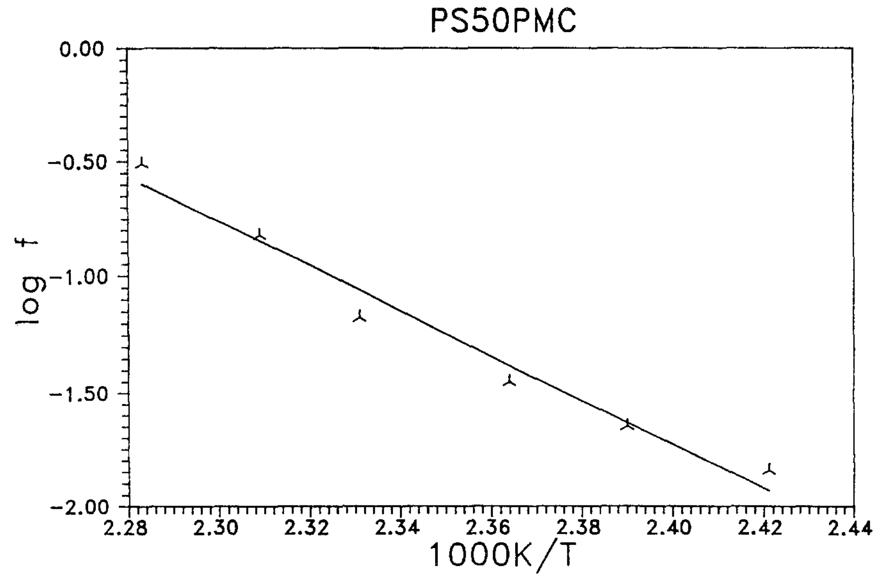


Fig. 6 Activation diagram of the ionic conductivity process observed in the 50:50 TMPC/PS blend

(>230 °C). However, direct measurements of the dielectric loss at this temperature range may lead to phase separation of the blend and therefore cannot be taken as a basis for the choice of frequency. The same information can be obtained by extrapolation of the ionic conductivity process observed in Fig. 2 to higher temperatures. This can be done on the basis of the activation energy and the slope values ($d\log \varepsilon''/d\log f$) of the ionic conductivity process. It is worth noting that the slope of the ionic conductivity process was almost the same for all temperatures, as can be seen in Figs. 2 and 5. An activation diagram of the ionic conductivity can be constructed by reading the frequency corresponding to an arbitrary loss value at different temperatures. The arbitrary value of the dielectric loss was taken equal to 0.1. Figure 6 represents the activation diagram of the ionic conductivity. According to the activation energy value obtained from Fig. 6 and the slope value (= − 1), the frequency dependence of the dielectric loss at temperatures 230° and 240 °C are extrapolated and presented in Fig. 5 as dashed lines.

It is now clear from Fig. 5 that the measurement at 10 kHz is good enough to allow precise measurement of the dielectric loss. The measurements at high frequency values are preferred since the higher the frequency the shorter the time of measurement. In addition, Fig. 3 shows that at this frequency and at temperatures above 200 °C, the glass process of pure TMPC (i.e., 100% phase separation of the blend) is quite far.

Accordingly, the variation of the dielectric loss with time was measured at 10 kHz using the same heating procedure described above at different temperatures, namely, 210°, 220°, 230°, and 240 °C. The results obtained are presented in Fig. 7. It can be seen in Fig. 7 that there is a rapid increase in the dielectric loss at the first 2 min. This increase could be attributed to the time required to attain the thermal equilibrium of the sample. This increase in the loss represents the normal behavior if the phase separation process is not taking place. However, this rapid increase is followed by a decrease in the loss values due to the spinodal decomposition of the blend. The rate of decrease in the dielectric loss value is strongly dependent on the temperature of measurements. It can also be seen that after a few minutes the decrease observed levels off, reaching equilibrium value. The time values obtained from Fig. 7 for equilibrium are in the same order of magnitude as those obtained by Illers et al. [4] and Guo and Higgins [8], i.e., 10 min at 250 °C using DSC measurements and 4 min at 240 °C using light-scattering method, respectively.

The rate constant of phase separation, k, can be determined using a simple decay equation:

$$\varepsilon''(t) = \varepsilon''(t = 0)\cdot\exp(-kt)\,, \qquad (2)$$

where t is time of measurement.

Figure 8 is the activation diagram of the phase separation process. The activation energy obtained is 46 kcal/mole. Although this value seems to be high, it is in the same order of magnitude as that obtained by Sato and Han [20] for PS/PVME blend and equals 37 kcal/mole. Sato and Han [20] obtained this value according to their determination of the molecular mobility constant at various temperatures. This agreement can be taken as a support for the results obtained by the current method since the different methods detecting the same process must deliver the same value of activation energy. For example, the activation curves of the glass process measured by different methods (dielectric, mechanical, NMR, Ultra

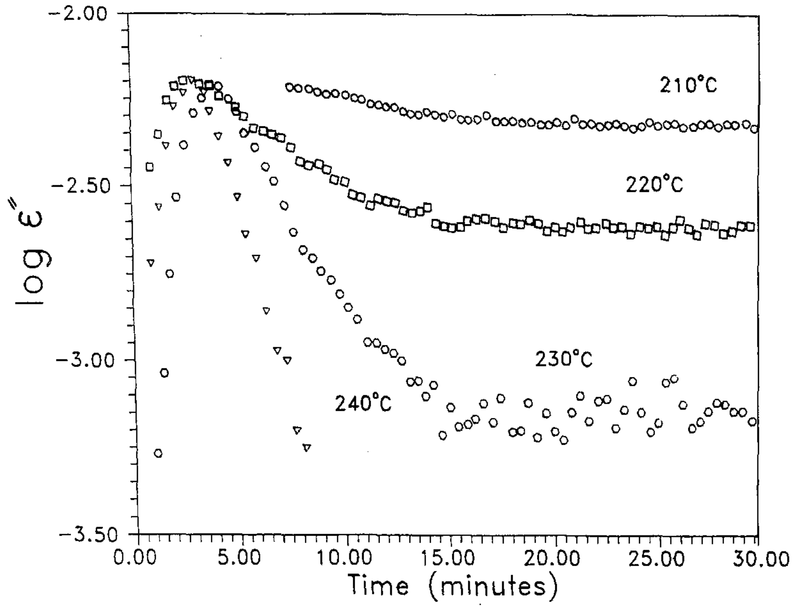


Fig. 7 Variation of the dielectric loss with time at different temperatures for 50:50 TMPC/PS blend

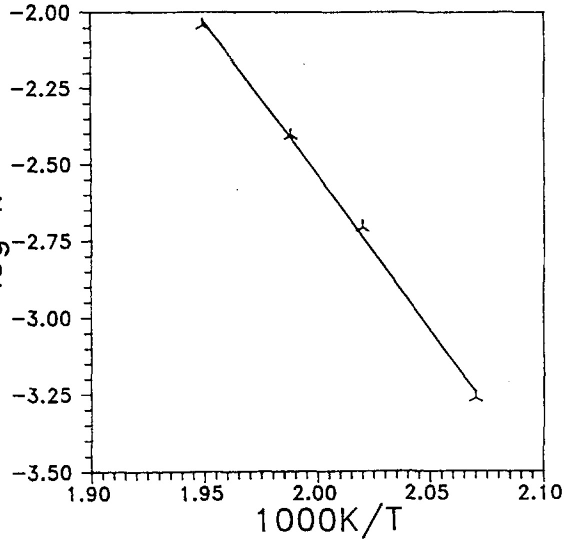


Fig. 8 The activation diagram of the phase separation process

sonic ...) for the same material are only parrallelly shifted on the frequency axis, i.e., have the same activation energy at the same temperature range [15, 21]. This is also valid for the local processes [15].

Determination of composition with time:

Although, the sample at temperatures above and below LCST exhibits only one ionic conductivity process, the decrease in the ionic conductivity at temperatures above LCST as a result of the phase separation process is mainly attributed to the progress in the formation of that phase, which has a greater glass temperature (higher viscosities). This phase (rich in TMPC) is responsible for the restriction of the ionic mobility. Furthermore, as the degree of phase separation increases not only the glass temperature TMPC-rich phase will increase, but also the size of the phase separated domains will increase, therefore leading to a greater hindrance of the ionic mobility. However, independent of the reason for the decrease in the ionic conductivity, the degree of phase separation can be correlated to the relative change in the loss value with time at a given temperature. Furthermore, the variation of the glass transition temperature of the TMPC rich phase with time can be determined from the dielectric loss/time measurements presented in Fig. 7. The values of $Tg(t)$ can be obtained in an approximate way if we neglect the slight shift from linearity observed in Fig. 4 by using the following equation:

$$Tg(t) = \frac{\varepsilon''(t = 0) - \varepsilon''(t)}{\varepsilon''(t = 0) - \varepsilon''(t = \infty)} \cdot \Delta Tg + Tg(\text{blend}) \,. \qquad (3)$$

The first term represents the increase in the glass transition temperature of the TMPC rich phase due to phase separation. Where $\varepsilon''(t = 0)$, $\varepsilon''(t)$ and $\varepsilon''(t = \infty)$, are the dielectric loss values at time equal to zero, at time t and after complete phase separation, respectively. ΔTg is the difference in Tg's between that of pure TMPC and that of a blend. The values of $\varepsilon''(t = 0)$ at every temperature can be directly obtained from Fig. 5 (as the value of ε'' corresponding to a frequency of 10 kHz). $\varepsilon''(t = \infty)$ is very small and can be neglected. The values of ΔTg and Tg can be obtained from the calorimetric measurements or from the dielectric activation curves as described before [17]. It was previously [17] found that not only the mechanical and

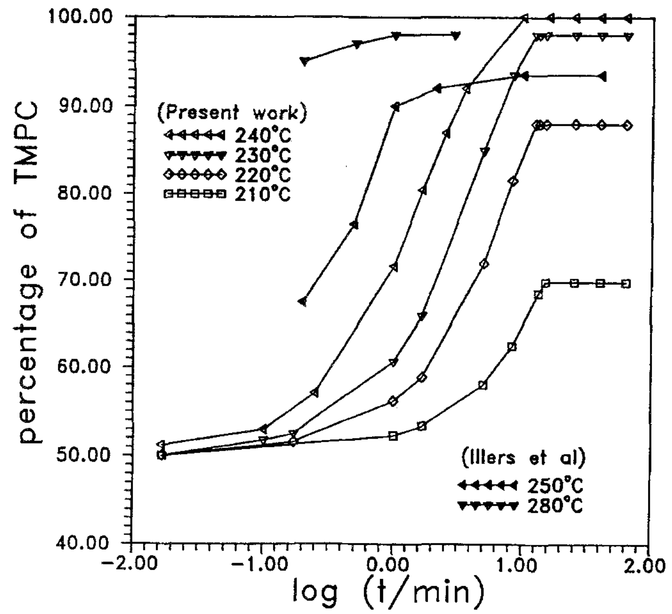


Fig. 9 Kinetics of phase separation of 50:50 TMPC/PS blend at different temperatures. The results of the temperatures 250° and 280 °C were obtained from ref. [4] (filled symbols), while the results of the present work are represented by open hollow symbols

dielectric activation curves, but also the dielectric and calorimetric glass temperatures are strongly correlated by a constant shift factor depending on the polymer. Accordingly, determination of the variation of composition by time was done by using the above equation to determine T_g and Fig. 4 to find out the corresponding composition ratios. The composition ratio values obtained for the different time intervals are plotted against the logarithm of time in Fig. 9. The hollow symbols represent the results obtained from Fig. 7 by the method described above, while the filled symbols are the results obtained by Illers et al. [4] using the quenching method. Illers et al. [4] determined the variation of composition for both TMPC- and PS-rich phases with the annealing time at two temperatures, i.e., 250° and 280 °C. This was done by annealing several samples with the composition 50:50 of TMPC/PS for different time intervals and then rapidly quenching the samples. Then, the glass transition temperatures were determined calorimetrically for both phases. The composition of the blend corresponding to certain annealing time was obtained from the glass transition temperature/composition diagram (similar to Fig. 4).

It is clear that the results obtained from the current method appear at the correct order regarding the temperature of measurements and the onset time. Moreover, the increase in the equilibrium concentrations of TMPC with increasing temperature is very similar to the behavior obtained by Illers et al. [4] as can be seen in Fig. 9. On the other hand, Illers et al. showed that samples annealed at 250° and 280 °C acquired a single phase when cooled and annealed at 220 °C. However, the last findings of Illers et al. and also the difference in the equilibrium concentration values between the dielectric and the light-scattering and calorimetric methods [4] can be attributed to the fact that each method detects another molecular level. This conclusion is supported by the results obtained by Kim and Paul [9]. They [9] constructed a phase diagram for the same blend using different methods, i.e., visual, light scattering, and DSC method. They found that the visual method gives higher temperature values (~255 °C) than the light-scattering method (~245 °C), which in turn gives higher values than that obtained from DSC measurements (~240 °C). The critical solution temperatures obtained from the dielectric measurements seem to have the lowest values (~210 °C) as the dielectric method detects smaller dynamical units, so that it is able to detect the phase separation at earlier stages than could be detected by the other mentioned methods.

Summary

Based on the above, it is possible to obtain important information about the kinetics of phase separation through real-time measurement and by using only one sample. The results obtained include the activation energy, rate constant, the onset temperature, and time of the phase separation. In addition, the results obtained are in good agreement and supported by the literature data. Furthermore, the present method delivers real time measurements and can be applied to the systems which are not conducive to quenching. On the other hand, this method has the disadvantage that it is not possible to detect the composition of the phase with the lower glass transition temperature (PS-rich phase in the present work). Finally, it can be stated that the present method seems to be a promising way to approach the complex subject of phase separation and the results obtained must be extended to other blend systems and compared also by other methods.

Colloid & Polymer Science, Vol. 273, No. 6 (1995)

References

1. Shaw MTJ (1974) Appl Polym Sci 18:449
2. Casper R, Morbitzer L (1977) Makromol Chem 581/59, 1
3. Yee AF, Maxwell MAJ (1980) Macromol Sci Phys 17:543
4. Illers K-H, Hechmann W, Hambrecht J (1984) Colloid Polym Sci 262:557
5. Okada M, Han CCJ (1986) Chem Phys 85:5317
6. Carmesin HD, Heerman DW, Binder K (1986) Z Physik B-65:89
7. Fernandes AC, Barlow JW, Paul DR (1986) Polymer 27:1788
8. Guo W, Higgins JS (1990) Polymer 31:699
9. Kim CK, Paul DR (1992) Polymer 33:1630
10. Alexandrovich PS, Krasaz FE, Macknight WJ (1980) J Macromol Sci–Phys, B17 (13):501
11. Yang H, O'Reilly JM (1987) Mater Res Soc Sym Proc 79:129
12. Breton MG, Fisher EW, Heckert-Maetzky C (1987) J Chem Phys 10:6144
13. Nagi KL, Ronald CM, O'Reilly JM, Sedita JS (1992) Macromolecules 25:3906
14. Mansour AA, Junge R, Stoll B, Pechhold W (1992) Colloid Polym Sci 270:325
15. McCrumm NG, Read BE, Williams G (1967) "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York,
16. a. Kronig RL (1926) J Opt Soc Am 12:547; b. Kramers HA (1927) Att Congr Fisic Como, 545; c. Böttcher CJ, Browdewijk P (1978) "Theory of Dielectric Polarization" Vol II, Elsevier Scientific Publ, Amsterdam
17. Mansour AA, Stoll B (1993) Colloid Polym Sci 271:834
18. Katana G, Kremer F, Fischer EW, Plaetschke R (1993) Macromolecules 26:3075
19. Zetsche A, Fischer EW (1994) Acta Polymer 45:168
20. Sato T, Han CC (1988) J Chem Phys 88:2057
21. Pechhold W, Grassel O, von Soden W (1990) Colloid Polym Sci 268:1089