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DDSC STUDIES ON IRIDESCENT POLYMER–AROMATIC SOLVENT SYSTEMS

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Abstract

Poly(2-hydroxymethyl methacrylate) (PHEMA) suspension in anisole shows temperature dependent iridescence between 0 and 60°C. To reveal the mechanism of the temperature-dependent iridescence, PHEMA–anisole mixtures were prepared, and their thermal behaviors have been studied by dynamic DSC (DDSC) technique. All the mixtures showed a broad peak at 325 K on loss part of DDSC curves (loss C_p curve), and showed a gentle step change between 250 and 340 K on the storage part (storage C_p curve). A temperature region of these changes matched the observation of iridescence change. Temperature of the step change depended on the composition of mixture. The temperature dependence of iridescence of the polymer mixture has been attributed to the conformational changes of PHEMA chains.

Keywords: DDSC, iridescence, phase separation, poly(2-hydroxymethyl methacrylate)

Introduction

Iridescence is sometimes observed in bilayer membranes, liquid crystals, surfactant systems, polymer suspensions, gel, and polymer solutions below the transition temperature [1, 2]. Iridescence can be explained to Bragg diffraction of visible light caused by an ordered structure or to the scattering of visible light caused by different density portions in the system. The temperature dependence of iridescence is observed below the phase transition temperature of the system, and it has been explained by the structural change of the system. Thermal analytic and calorimetric techniques have been used in the study of iridescent systems. In the temperature-dependent iridescence system, assuming structural change of the system reflects the change of color is not difficult. An endotherm that corresponds to phase transitions was observed above the temperature where iridescence color changes in surfactant mixtures and in polymer solutions [1, 3]. It is well known that mixing of a low molecular mass compound to a polymer lowers the glass transition temperature of the polymer [4]. Although the structural change of a polymer chain should be correlated to the temperature dependence of iridescence, DSC studies of this region were very little [5, 6]. We reported that PHEMA suspension in several aromatic solvent shows temperature-dependent iridescences. The mechanism of iridescence was explained

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by the specific scattering of light [2]. Secondary transitions of PHEMA were studied by dynamic mechanical measurement, and effects of small molecules such as water on the transitions were measured [7, 8]. Although anisole is not a good solvent for PHEMA, the ether group on this solvent molecule may affect the structure of PHEMA chains. Therefore, thermodynamic change of PHEMA chains in the polymer–solvent mixture may be observed in this system. Recently, a temperature-modulated DSC (DDSC or TMDSC) has been developed and used for the studies of systems where several phenomena appear at the same temperature region [9–11]. Since DDSC gives us in-phase and out-of-phase information that dynamic mechanical analysis does, we expect that this technique will give us better sensitivity and more information than conventional DSC or other calorimetry. In this paper, we report the DDSC results of PHEMA–anisole system at the temperature region where system changes its iridescent color.

Experimental

Materials

PHEMA (M_m=30 000) was obtained from Aldrich Chemical Co., Inc. This polymer was dissolved in methanol, and its polymer film was made from the solution. After drying, the film was powdered by mortar. Anisole was obtained from Wako Pure Chemical Ind., Ltd., and dried over molecular sieves 4 Å for a week.

Methods

To prepare a 1:1 mixture, 10 mg of PHEMA and a 10 ml portion of anisole were placed in a stainless steel pan. The pan was tightened by a stainless steel cover and an O-ring. To find the steady state condition of dipping of the polymer, the samples were kept at room temperature from several to 100 h before the measurements. DDSC experiments were carried out in a Perkin Elmer DSC7 equipped with a DDSC kit. Baseline data for DDSC experiments were corrected using both empty pan and anisole-contained pan. DDSC curves were obtained in both iso-scan mode and heat-cool mode. In iso-scan mode, repeating units is composed of an isotherm followed by a 2 K scan segment. In heat-cool mode, repeating units is composed of a 4 K heat segment followed by a 2 K cool segment. Each segment was set to 30 or 60 s. The measurements were carried out between 243 and 403 K. Storage C_p curves and loss C_p curves were calculated from the heat-flow curves by the software.

Results and discussion

DDSC curve of PHEMA–anisole

Figures 1 and 2 show the DDSC curves of PHEMA–anisole (1:1) mixture obtained in iso-scan mode and heat-cool mode, respectively. In Fig. 1a, a step change was observed on both storage C_p curves. The onset and offset temperatures of PHEMA–anisole were at lower temperature than the glass transition temperatures of PHEMA (T_g=378 K). An exotherm peak at 355 K appeared on storage C_p curve of most PHEMA–anisole. At the same temperature, an endotherm peak appeared on the loss C_p. The exotherm peak on the storage C_p curve is probably due to unsuccessful separation of the loss component caused by a first order phase transition such as phase separation. In heat-cool mode, a step change appeared on the storage C_p curve, and the transition temperature was almost the same that obtained in iso-scan mode.

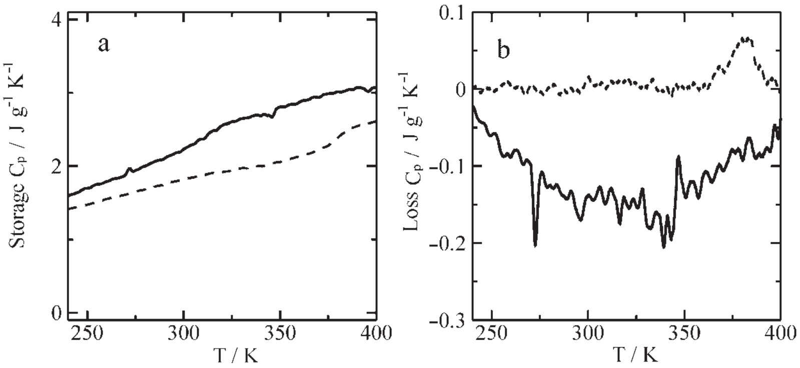

Fig. 1 DDSC curves of dried PHEMA (solid line) and PHEMA–anisole 1:1 mixture (dashed line) measured in iso-scan mode. a – storage C_p curve; b – loss C_p curve. Heating 2 K followed by 60 s isotherm

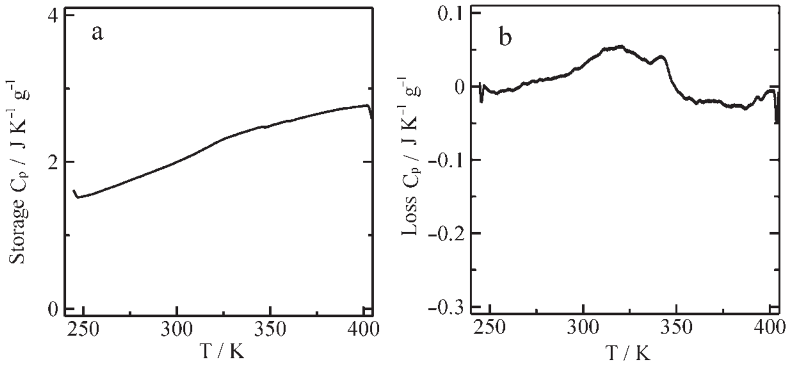

Fig. 2 DDSC curves of PHEMA–anisole 1:1 mixture measured in heat-cool mode. a – storage C_p curve; b – loss C_p curve. Heating 4 K followed by cooling 2 K. Scan time is 30 s

The loss C_p curves obtained by iso-scan mode were very complicated. Figure 1b shows many endo- and exotherm peaks. The peak at 273 K corresponds to melting of ice. The most of the others may look like instrumental noise. However, large peaks in the temperature region between 325 and 375 K were observed only in the mixtures. DDSC curve of PHEMA showed small peaks. Since reproducibility of these small peaks was poor compared to those observed in mixtures, they are considered the experimental noise under this condition. A broad peak and a small peak appeared on the loss C_p curve in Fig. 2b at 320 and 340 K, respectively. In our iridescent system, phase separation must be observed. The small endotherm peak may be attributed to the phase separation of the system because this system becomes completely opaque over 340 K.

Dependence of the thermal behavior of PHEMA–anisole on the composition

Figure 3 shows plot of onset temperature T_{onset} *vs*. composition of mixtures. This plot shows that the presence of anisole lowers the onset temperature of the system. This relationship seems similar to what is observed between glass transition temperature and composition of copolymer or composition of compatible polymer blends. However, this plot did not fit the calculated curve based on the Fox equation [4]. Our experimental results suggest that compatibility of PHEMA and anisole is moderate. Interaction between the OH group of PHEMA and ether group of anisole must be important in this moderate compatibility.

Table 1 Thermal behaviors of PHEMA–anisole

No.	PHEMA: anisole[a]	Storage C_p			Loss C_p		
		T_{onset}/	T_{offset}/	ΔC_p/	T_{onset}/	T_p/	ΔH/
		K		$J\ g^{-1}\ K^{-1}$	K		$J\ g^{-1}$
1	1:1[b]	307	316	0.18	–	–	–
2	1:1[b,d]	305	314	0.16	293	321	2.4
3	1:1[c]	313	330	0.14	307	327	2.6
4	2:1[c]	315	330	0.12	289	325	8.7
5	3:1[c]	324	333	0.04	303	335	8.8
6	1:0[b]	372	385	0.21	362	384	1.3

[a] Ratio in mass. Amount of anisole in each sample is 10 mg
[b] 2 K/step, 2 K min^{-1}, scan time=60 s
[c] Heating 4 K at 10 K min^{-1}, cooling 2 K at 5 K min^{-1}
[d] Sample mass: 5 mg of PHEMA and 5 mg of anisole. Reference mass: 5 mg of anisole

Table 1 summarizes thermodynamic properties of PHEMA–anisole to the sample composition. The T_{onset} of No. 3 is relatively higher than that of No. 1, although their compositions are the same. This is due to the difference of under-heating rates between heat-cool mode and iso-scan mode. The DC_p varied between 0.14 and 0.04 $J\ g^{-1}\ K^{-1}$ depending on the composition. As the DC_p is strongly affected by the shape of the sample, explaining this tendency only from the presented data is difficult. However, the decreasing of the DC_p with increasing the ratio of the PHEMA may suggest the increase of association of the PHEMA that increase the density of the polymer domain. The ΔH values of PHEMA–anisole calculated from the loss C_p curves is relatively large comparing with PHEMA. The thermal conductivity of the

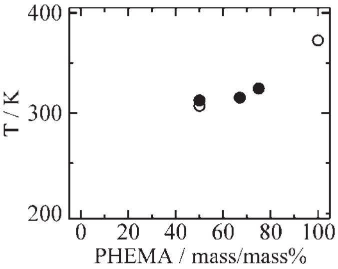

Fig. 3 Transition temperatures of PHEMA–anisole mixtures in different compositions: Data from iso-scan mode (o) and heat-cool mode (●)

PHEMA–anisole may be lower than PHEMA, and this may increase the ΔH with increasing the amount of the sample. If so, this value should depend on the amount of the sample. In Table 1, No. 4 and No. 5 may be explained by the difference of thermal conductivity. However, ΔH of sample No. 3 is almost equal to No. 2, although amount of the No. 3 is almost half of No. 2. Lednický and Janáček found a relaxation process of the side group of PHEMA near 303 K by dynamic mechanical analysis [7]. They explained this process to the fact that the hydroxyl group of the side group interacts with an ester group in proximity to main chain. This interaction may be the reason for relatively large ΔH of PHEMA–anisole.

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