

Polymer Communication

Selective plasticization in electroluminescent block copolymers

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Received 26 July 1999; received in revised form 28 December 1999; accepted 9 February 2000

Abstract

Differential scanning calorimetry (DSC) measurements of glass transition temperature (T_g) and of changes in heat capacity at T_g have been made on a series of electro-optically active alternating block copolymers of systematically varying hard and soft block structures and of their blends with the plasticizer, 1,12-dibromododecane (DBDD) in order to assess the nature of phase separation in these copolymers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymers; Plasticization; Differential scanning calorimetry

1. Introduction

Polymers containing alternating conjugated and nonconjugated sequences have been studied in terms of their electro-optical properties, including electrical conductivity [1], nonlinear optical activity [2] and electroluminescence (EL) properties [3,4], and compared to those of nominally fully conjugated polymers such as polyacetylene, poly(*p*-phenylene) and poly(*p*-phenylene vinylene) [5,6]. In the organic EL field, these amorphous structures have been termed alternating block copolymers [7–9]; though clearly there can be semantic ambiguity we shall follow this practice here. Such copolymers are intrinsically soluble, have good film forming and mechanical properties and are suitable for fabrication of devices [10–15]. The copolymers used in the present study contain short substituted phenylene vinylene sequences separated by methylene spacer groups in their structure. These copolymers were synthesized as described previously [10,14]. The molecular structures of model compounds (copolymers **2**₈, **3**₈ and bmppv) are shown in Fig. 1. The structures of **2**₈ and **3**₈ but not of bmppv could be regarded as homopolymers; however, because of profound structural differences between the hard aromatic and the soft aliphatic sequences (which we will term blocks in the following) in these chains, it might be anticipated that full or partial phase segregation may occur.

More conventional hard/soft alternating block copolymers are typified by certain polyurethanes [16–20], and

these copolymers have been often studied in terms of their phase behavior. The two respective blocks are often at least in part immiscible and in many cases lead to segregation in the equilibrium structure. If two amorphous phases are then present, they may be detected by their individual glass transition temperatures, T_{gs} (measured calorimetrically and/or dynamic mechanically) and also microscopically. A full analogy to segmented polyurethanes is clearly inappropriate, as the separate blocks in the conjugated/nonconjugated polymers used here are much shorter than those encountered in polyurethanes. Further, in contrast to the typical segregated block polyurethane, only a single T_g has been observed in the present systems.

A further relevant comparison may be made to certain ionomers [21,22] in which the dissimilarity of the underivatized segments and of the ion-containing segments is so large that clusters or domains of the latter are formed. In this case also two T_{gs} can be observed, reflecting the presence of the phase separated domains and the matrix, respectively [21,22]. It seems that the requirement for phase separation is not necessarily long block length but rather flexible chain containing two highly dissimilar segments. For some polyurethanes and for some ionomers, therefore, thermal measurements provide a useful diagnostic tool for investigating microphase behavior.

For the present systems it has already been shown that T_g drops systematically as the soft block length increases [10]. Although it is tempting to ascribe the observed drop in T_g of the covalently anchored methylene sequences as their length increases, as being typical of the behavior of domains of essentially pure methylene sequences, there is an alternative explanation, namely, that there is phase homogeneity in

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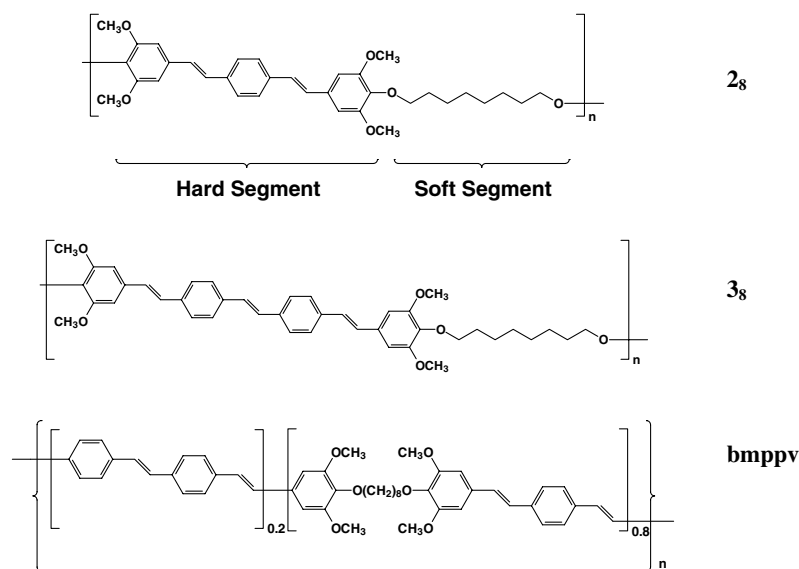


Fig. 1. Molecular structure of typical EL block copolymers (2_8 , 3_8 and bmppv).

these systems and the drop in T_g merely reflects the increase diluent content of the homogeneous hard/soft block mixture.

The purpose of this study was to determine the extent of microphase separation, if any, occurring in the above copolymers. This was carried out by: (a) quantitative determination of the thermal transition parameters of the copolymers as a function of structure; and (b) by a study of selective plasticization of the soft block by a low molecular weight diluent, 1,12-dibromododecane (DBDD)—chosen for its chemical similarity to the methylene sequences and its dissimilarity to the π -conjugated phenylene vinylene hard blocks. DBDD is a nonsolvent for the block copolymer

itself; however, it is found to be an effective plasticizer in depressing the observed T_g of these systems.

2. Experimental

2.1. Materials and molecular characterization

Six electro-optically active alternating copolymers (designated 2_6 , 2_8 , 2_{10} , 2_{12} , 3_8 and bmppv, Table 1) consisting of short substituted phenylene vinylene sequences interspersed with optically inert oligomethylene blocks were

Table 1
Molecular characterization and DSC results of electroluminescent block copolymers and their blends with dibromododecane (DBDD)

Samples	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n^a	Composition DBDD (%) (w/w) ^b	T_g (°C) ^c	ΔC_p (J/g°C) ^d
<i>Copolymers</i>						
2_6	21.9	8.68	2.52		90	0.17
2_8	27.3	10.7	2.55		80.9	0.25
2_{10}	24.1	8.63	2.79		68.5	0.25
2_{12}	29.3	11.2	2.62		61.1	0.35
3_8	8.63	4.70	1.83		78.7	0.06
bmppv	18.3	7.75	2.36		78.6	0.27
<i>Blends 2_8/DBDD</i>						
A				1.82	70.9	0.26
B				2.75	67.9	0.28
C				5.10	64.2	0.29
D				7.98	47.0	0.43
E				9.49	51.5	0.35
F (3_8 /DBDD)				8.04	57.5	0.09
G (bmppv/DBDD)				7.82	56.9	0.33

^a Via GPC.

^b Weight percentage of plasticizer (DBDD) in blends with copolymers (2_8 , 3_8 and bmppv).

^c T_g was taken at onset of the corresponding heat capacity jump.

^d ΔC_p is the observed heat capacity change per unit mass of sample for copolymers and blends.

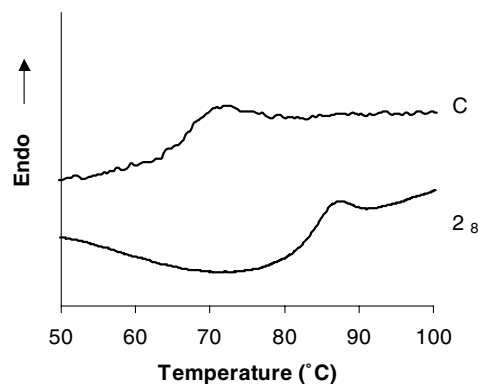


Fig. 2. DSC of copolymer 2_8 and of blend C with DBDD (see Table 1), (second heating run, 20°C/min).

synthesized as previously described [10]. In the first four of members of this copolymer series, the hard block structure remains constant while the length of the soft, methylene block is varied systematically (the number of methylene units is designated by the subscript). The copolymer 3_8 contains an additional phenylene vinylene unit, and was added to afford a further comparison, while bmppv is a more random structure in terms of the length of its hard block but contains an invariant soft block of eight methylene units (Fig. 1.)

1,12-Dibromododecane, (Aldrich) was recrystallized from absolute ethanol. The blends of the EL copolymers

Table 2
Calculated heat capacity changes ($\Delta C_p^{(s)}$ or $\Delta C_p^{(ts)}$) for copolymer and blend samples

Samples	Total content of soft phase (%) (w/w)	DBDD content in total soft phase (%) (w/w)	$\Delta C_p^{(s)}$ (J/g°C) ^a	$\Delta C_p^{(ts)}$ (J/g°C) ^b
<i>Copolymers</i>				
2_6	16.3	–	1.05	–
2_8	20.6	–	1.20	–
2_{10}	24.5	–	1.03	–
2_{12}	28.0	–	1.26	–
3_8	17.3	–	0.35	–
bmppv	19.2	–	1.39	–
<i>Blends 2_8 /DBDD</i>				
A	22.0	8.3	–	1.18
B	22.8	12.0	–	1.24
C	24.6	20.7	–	1.16
D	26.9	29.6	–	1.59
E	28.1	33.7	–	1.25
F(3_8 /DBDD)	24.0	33.5	–	0.38
G(bmppv/DBDD)	25.5	30.6	–	1.27

^a Heat capacity change per gram of soft blocks in copolymers calculated using relation $\Delta C_p^{(s)} = \Delta C_p^{\text{observed}}/\text{weight fraction of soft blocks in the copolymers}$.

^b Heat capacity change per gram of total amorphous phase including DBDD calculated using relation $\Delta C_p^{(ts)} = \Delta C_p^{\text{observed}}/\text{weight fraction of total amorphous phase in the blends}$.

with DBDD (see Table 1 for compositions) were prepared by solvent casting the mixture from chloroform. The blend films (A–G) were dried under vacuum for at least 48 h till constant weight.

Gel permeation chromatography (GPC) measurements were recorded using a Waters Model 590 with Waters 410 Differential Refractometer. The solvent THF at flow rate of 1 ml/min at 30°C and Water Styragel columns (HR5, HR4, HR3) were used. Polystyrene standards (Polymer Laboratories Ltd., UK) were used in calibration.

2.2. Differential scanning calorimetry

DSC data for all the copolymers and the blends were obtained with a Perkin–Elmer DSC-7 using Pyris Software. Indium, mercury and tin were used for calibration. The samples were scanned from –50 to 150°C with a heating rate 20°C/min. The glass transition temperatures were taken as onset temperature of the heat capacity jump, ΔC_p . At least four sequential scans were carried out for each sample. After heating to 150°C the samples were cooled at 5°C/min to ambient temperature. The data shown in Fig. 2, Tables 1 and 2 refer to second scans which were identical to subsequent scans. No heating or cooling rate effects were observed because the heating protocol itself served to anneal the samples.

3. Results and discussion

Observed transition temperatures and the associated ΔC_p s for the copolymers and for their blends with DBDD are presented in Table 1. A typical DSC thermogram (Fig. 2) shows the change in T_g for the copolymer 2_8 and blend C. DBDD concentration (weight percentage of DBDD in total amount of sample) was kept below 10% (w/w); above this concentration, phase separation of the plasticizer occurred as evidenced by a large endotherm at 40°C corresponding to the melting point of free plasticizer.

Fig. 3 shows T_g as a function of the number of methylene units in the nonconjugated spacer blocks (x). The observed monotonic decrease is consistent with previous work [10] which attributed this glass transition to the segregated soft block in the copolymers. A comparison of the present and earlier data [10] shows differences of a few degrees which may reflect the essentially arbitrary choice of T_g assignment in a somewhat smeared C_p plot. A similar study of T_g vs. soft block length was reported recently for liquid crystalline polymers with phenyl substituents of the arylene vinylene segment and different numbers of methylene units in the flexible spacers. In this case the single T_g showed a discontinuous drop for polymers with long flexible spacers [23] containing more than six methylenes and this result is in agreement with the present work which studied blocks ranging from 6 to 12 methylenes.

We note that the copolymers containing the same number of methylene units, (i.e. copolymers 2_8 , 3_8 and bmppv) exhibit identical glass transition, 79°C, within an experimental error

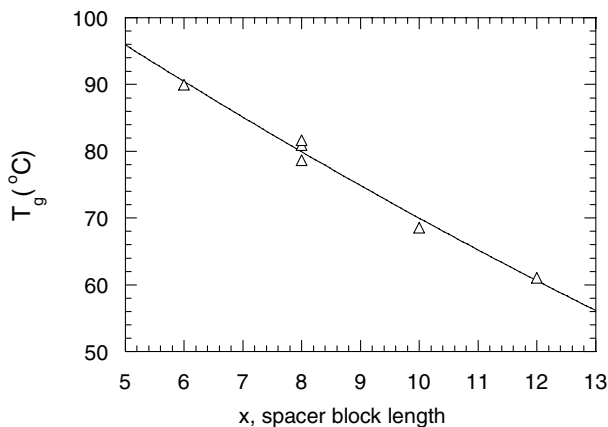


Fig. 3. Glass transition temperature of copolymers as a function of spacer block length.

of $\pm 2^\circ\text{C}$. The fact that the T_g is determined only by the soft block length and not by the nature of the hard block or the relative amount of soft block (see Table 1) is consistent with the presence of a phase-separated soft block. The absence of any observable thermal transition in these copolymers that can be associated with the hard block reflects the fact that such transitions would occur only above the decomposition temperature.

The supposition that phase segregation occurs in these systems is supported by the observation of selective plasticization behavior. The plasticizer used, DBDD is a nonsolvent for the block copolymers but its chemical structure implies that a selective solvation of the soft block is credible. Such selectivity in solvation or plasticization is common in diblock systems [24–28] but has been less

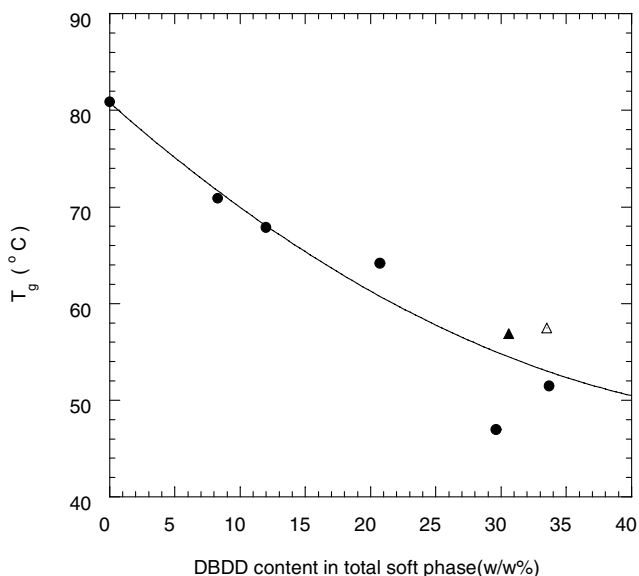


Fig. 4. Glass transition temperature of the copolymers and blends vs. plasticizer content (copolymer 2_8 and blends A–E (●), blend F (Δ) and blend G (▲)).

frequently studied in multiblock structures. An example of selective plasticization in diblock copolymer is given by Nojima et al. [24], in which standard plasticizers were used to selectively lower the T_g of the styrene blocks in ϵ -caprolactone–styrene diblock copolymers.

In the present work we were able to observe a systematic decrease in the copolymer T_g s with increasing content of DBDD. Fig. 4 shows these decreases for several copolymer blends; again, the changes appear to be independent of the hard block. That is, the data show a uniform monotonic decrease on the addition of plasticizer of an eight-methylene unit soft block, regardless of the nature of the hard block. In Fig. 4, total soft phase content is calculated on the assumption of a complete hard/soft block separation and includes DBDD (Table 2, column 3). Further quantitative assessment is provided by analysis of C_p changes at the glass transition of the pure copolymers and of the blends. Fig. 5 shows that the magnitude of the step change in the specific heat, ΔC_p , accompanying the soft segment glass transition increases with increasing weight percentage of total amorphous phase that includes soft methylene blocks of the copolymers and the DBDD plasticizer. ΔC_p for 3_8 is unusually low, as can be seen in Table 1, and the data for this polymer is omitted in Fig. 5. The reason for this anomaly is under investigation. In Table 2, we have calculated the $\Delta C_p^{(s)}$ at T_g of the soft block for the 2_x copolymer series from the data, again assuming complete phase separation occurs. Within experimental error, the results are constant, $1.14 \pm 0.09 \text{ J/g}^\circ\text{C}$. A similar calculation for the 2_8 blends with DBDD yields $1.28 \pm 0.15 \text{ J/g}^\circ\text{C}$. The change in heat capacity at T_g for DBDD is not known but it is presumably higher than that of the soft block and therefore accounts for the difference in these two values. The constant values in both cases based on an excluded amorphous phase assumption, together with T_g results, lend validity to the concept of soft block segregation and selective plasticization. The domains can be expected to be quite small and for the systems studied here were not detectable by either scanning or atomic force microscopy. We note that an aggregation of chromophores in a copolymer system has been postulated on spectroscopic evidence by Faraggi et al. [29].

4. Conclusions

The present work distinguishes between a phase segregated and nonsegregated model for a conjugated and nonconjugated multi-block alternating copolymer. Although the sequences are relatively short, the results of measurements of T_g and ΔC_p of the copolymers blended with plasticizer miscible only with the nonconjugated block favor a segregated model.

Acknowledgements

The authors of this paper would like to thank the Air

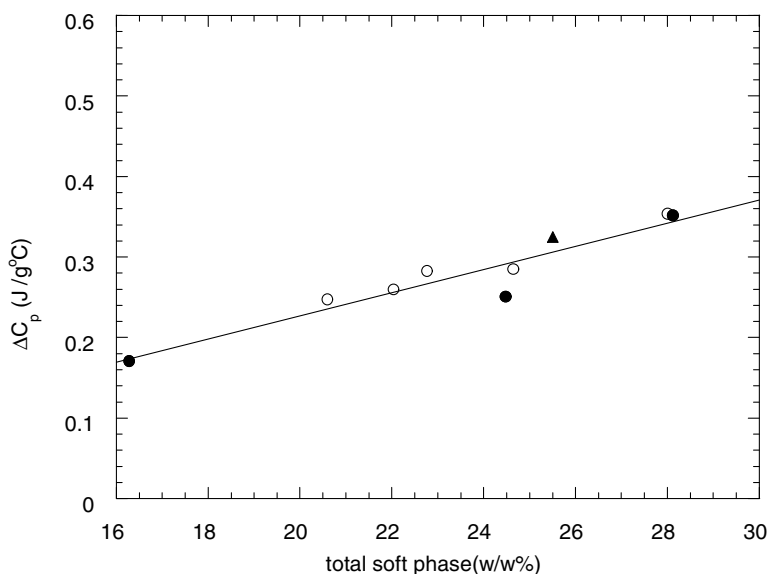


Fig. 5. Plot of observed heat capacity change for copolymers and blends ($2_6, 2_{10}, 2_{12}, 2_8$) (●), 2_8 and blends A–E (○) and blend G (▲).

Force Office of Scientific Research (Grant No. F 49620-99-1-002) and Osram-Sylvania Inc. for financial support.

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