ELSEVIER

S0032-3861(96)00297-2

Polymer Vol. 37 No. 23, pp. 5159–5163, 1996

0032-3861/96/$15.00 + 0.00

Dynamic viscoelastic properties of poly(ethylene–propylene) diblock copolymer in the melt state and solutions

Kazuo Sakurai* and William J. MacKnight†
Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA

and David J. Lohse, Donald N. Schulz and Joseph A. Sissano
Corporate Research Laboratories, Exxon Research & Engineering Company, Annandale, NJ 08801, USA

and Wolfgang Wedler and H. Henning Winter
Chemical Engineering Department, University of Massachusetts, Amherst, MA 01003, USA
(Received 18 October 1995)

Dynamic mechanical properties of a symmetrical poly(ethylene–propylene) diblock copolymer with a molecular weight of 99×10^3 were investigated in the melt state, as well as in solutions in 1,2,4-trichlorobenzene. In the melt state, the frequency dependence of the elastic and loss moduli (G' and G'', respectively) exhibited a limiting behaviour of $G' \approx G'' \approx \omega^{0.5}$ in the terminal zone, a marker of inhomogeneity. Even solutions of 15 vol% polymer showed such inhomogeneity. These rheological data indicate that the diblock polymer is microphase separated and the phases are strongly segregated. The limiting behaviour in the terminal zone suggests that a lamellar structure is present in the melt. Copyright © 1996 Elsevier Science Ltd.

(Keywords: dynamic mechanical; poly(ethylene–propylene)diblock copolymer; melt)

INTRODUCTION

Block copolymers have been shown to exhibit an order–disorder transition (ODT) with increasing temperature or decreasing molecular weight[1–4]. In the context of the random phase approximation (RPA)[4], ODT is defined as the point where the structure factor, $S(q)$, has a maximum at a certain length, while it remains zero at infinite length. The RPA theory also predicts the critical point for symmetric block copolymers given by [4]

$$(\chi N)_c = 10.5 \qquad (1)$$

Here, χ is the Flory interaction parameter and N is the total number of statistical segments for the block copolymer. Since $S(q)$ is identical with the scattering function, appearance of the maximum of $S(q)$ corresponds to the formation of periodicity in the structure. From the morphological point of view, the ODT corresponds to the formation of microphase separation in block copolymers, and these microdomains come to align periodically. Lamellar, cylindrical, and spherical structures have been observed for the domain structures, depending on the ratio of the volume fraction for the blocks[5,6]. In the ordered state of block copolymers, the rheology has been shown to display characteristic behaviour which depends on the microphase structures[2,3,7]. For lamellar structures, the following relation has been shown to apply in the terminal zone both experimentally[2,3] and theoretically[8]:

$$G' \approx G'' \approx \omega^{0.5} \qquad (2)$$

This relation is in contrast to the terminal zone behaviour for monodisperse homopolymers which is $G' \approx \omega^2$ and $G'' \approx \omega$. Since the changes in the terminal zone are so marked, they can be used as a criterion to determine the ODT[1,2].

In this series of papers[9] we have studied blends of poly(ethylene–propylene) diblock (DEP) copolymers and polypropylene, and have speculated that DEP forms a lamellar structure in the melt state for $M_w \approx 100 \times 10^3$. Neither small angle X-ray scattering (SAXS) nor transmission electron microscopy (TEM) were feasible in this case because the electron density difference was too small to provide the contrast between APP and PE in the melt state. Although not a direct method for determining morphology, rheological behaviour can provide some evidence for the presence of microphases in block copolymers. This paper will discuss the dynamic mechanical properties of DEP and its solutions with 1,2,4-trichlorobenzene (TCB), and we will attempt to evaluate the extent of segregation for this sample.

---

* Permanent address: Research and Development Center, Kanebo Ltd., 1-5-0- Tomobuchi-cho, Miyakojima-ku, Osaka, Japan

† To whom correspondence should be addressed

Table 1 Nomenclature and molecular characteristics

Sample	Nomenclature	M_w^a	M_w/M_n^a	Polyethylene content^b (wt%)	Ethyl branch content^c (mol%)	T_g (°C)
Ethylene–propylene diblock copolymer	DEP99	99,100	1.07	50 $f = 0.50^d$	3.0	−2.0
Atactic polypropylene	APP15	15,100	1.05	0	–	−2.0
	APP39	39,300	1.04	0	–	−3.0
Polyethylene	PE43	43,000	1.10	100	3.0	

^{a} Calculated from unhydrogenated precursors' results which were measured by gel permeation chromatography with low-angle laser light scattering. The calibration was done by standard polybutadiene samples

^{b} From ^{13}C n.m.r.

^{c} From ^{13}C n.m.r. and *FT*i.r. (in PE block for DEP)

^{d} Symmetry factor defined as ethylene composition (vol%) in DEP calculated assuming the density of b-PE in the melt state to be 0.865 g cm^{-3}

EXPERIMENTAL

Samples

The samples of DEP, atactic polypropylene (APP), and polyethylene (PE) were prepared by hydrogenation of anionically synthesized poly(1,4-butadiene-*b*-2-methyl-1,3,-pentadiene), poly(2-methyl-1,3-pentadiene), and poly(1,4-butadiene) respectively. The details for the preparation of DEP and APP have been described previously[9,10]. Molecular weights, branch contents, and other molecular characteristics for these samples are listed in *Table 1*, as is the nomenclature used in this paper. We also examined TCB solutions of DEP at concentrations of 50 and 15 vol% of polymer, hoping to find the order–disorder transition. TCB is a good solvent for both polyethylene and polypropylene, so DEP99 should be dissolved above the melting temperature of PE and, we expected, the solvation would reduce the segmental interaction parameter.

Rheometry

Dynamic elastic and loss moduli, G' and G'', were measured with a Rheometrics Dynamic Spectrometer RDS-7700 operated in the oscillatory mode between 0.01 and 100 rad s^{-1} using 25 mm-diameter parallel plate fixtures. Thermally regulated nitrogen gas was continuously circulated in the environmental chamber to maintain the temperature of the plates to within ± 1 K. The plate to plate gap was kept at 1-mm by adjusting the apparatus at each temperature. Measurements were performed in the linear viscoelastic regime with a maximum shear strain amplitude of 10%.

Two different types of experiment were carried out in characterizing rheological properties for DEP, isochronal temperature scans and isothermal frequency scans. The first set of experiments involves measurement of the elastic moduli of DEP99 and its TCB solutions at 10 rad s^{-1}. The second set of experiments was a conventional isothermal frequency scan. This was conducted for APP39 and APP15 in the temperature range of 10–206°C and for PE43 and DEP99 in the temperature range of 100–206°C which are above the melting temperature of PE. Elastic and loss moduli were superimposed assuming that the time–temperature superposition principle was applicable to all systems, and 140°C was taken as the reference temperature.

RESULTS AND DISCUSSION

Frequency dependence of moduli

Figure 1 shows the frequency dependence of the dynamic moduli for the three homopolymers, APP15, APP39, and PE43. For APP15 and APP39 the data exhibited features in the terminal and plateau zones typical for monodisperse homopolymers. For PE43, since the temperature range was far above the glass transition, the data showed only a part of the terminal zone. The frequency dependence of G'' for PE43 deviates somewhat from the expected slope of 1. The reason for this deviation is not clear, since the molecular weight distribution is narrow enough to give the expected slope in the terminal zone. However, this phenomenon is commonly observed for high molecular weight samples of hydrogenated polybutadiene[11].

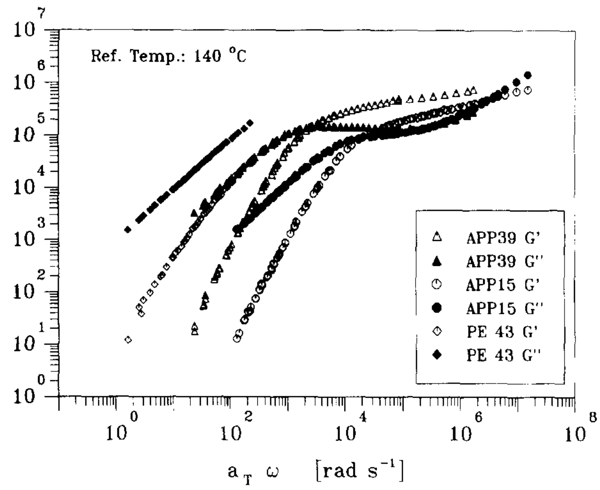

Figure 1 Reduced dynamic elastic and loss moduli (G' and G'', respectively) for homopolymers APP39, APP15 and PE43. Superposition was done taking the set of data at 140°C as a reference

Figure 2 presents master-curves of the frequency dependence of G' and G'' for DEP99. Superposition appeared to be valid within experimental error, and the dynamic elastic and loss responses at low reduced frequencies exhibited a limiting frequency dependence of about $G' \approx G'' \approx \omega^{0.5}$. This feature indicates the presence of very long relaxation times. As these are much longer and more distributed than for both homopolymer APP and PE, it suggests that DEP99 is not homogeneous but microphase-separated. According to the experimental results of Bates and coworkers[2,3], as well as the theoretical calculation by Rubinstein and Obukhov[8] for microphase separated diblock copolymers, the exponent of 0.5 for both elastic and loss moduli at the low frequency limit is characteristic of the presence of a lamellar structure. Therefore the low frequency behaviour of the modulus of DEP99 suggests that DEP99 microphase separates and forms a lamellar structure in the melt state. This

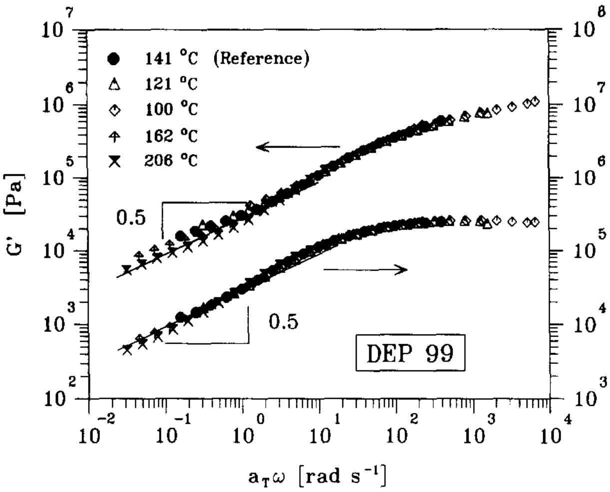

Figure 2 Frequency dependence of G' and G'' for diblock copolymer DEP99

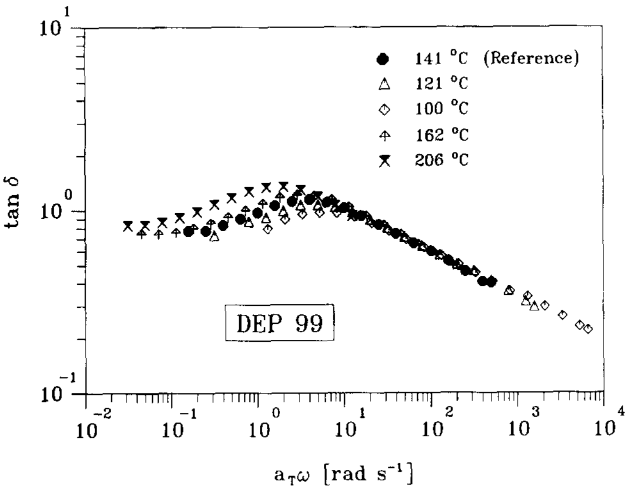

Figure 3 Frequency dependence of tan δ for DEP99

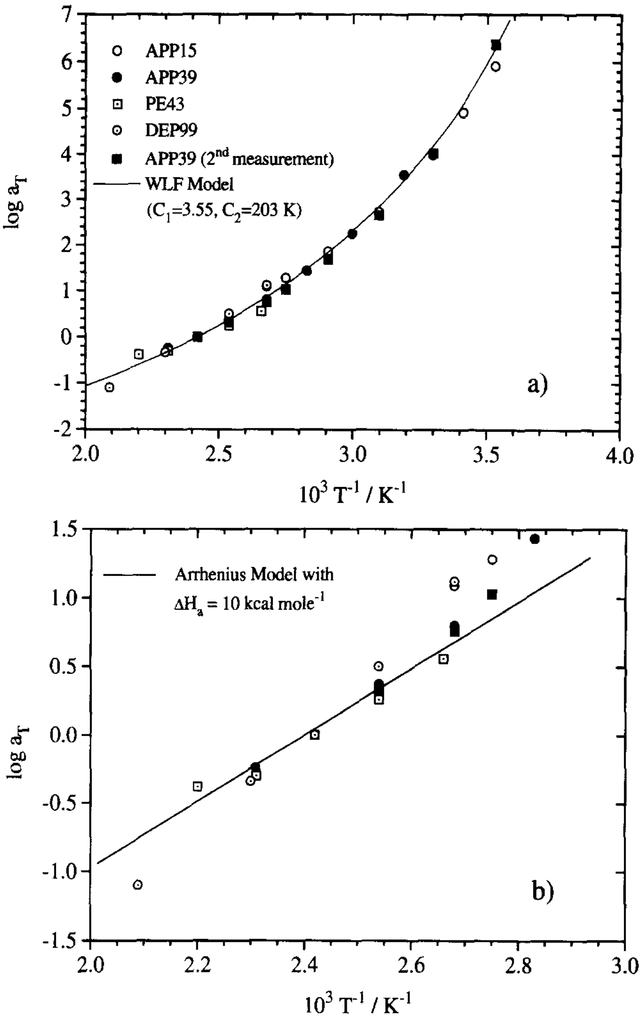

Figure 4 Temperature dependence of the shift factor a_T for APP15, APP39, PE43, and DEP113. The solid curve in (*a*) is calculated from the WLF equation with $c_1 = 3.55$ and $c_2 = 203$ K, and the solid line in (*b*) corresponds to the Arrhenius equation with $\Delta H = 10$ kcal mol^{-1}

speculation is consistent with the fact that an almost equal volume fraction of PE and APP in DEP99 (see *Table 1*) is favourable for formation of lamellae.

The G' and G'' data of *Figure 2* suggest the validity of the time–temperature superposition principle in our data. However, the more sensitive tan δ data cannot be superimposed. Its maximum shifts to lower reduced frequencies with increasing temperature as shown in *Figure 3*. This fact may be explained by postulating that increasing temperature induces some minor structural changes in the lamellae. Small angle neutron scattering (SANS) from a different sample of DEP supports the temperature effect of the domain structures[12]. We measured SANS from a DEP sample for which $M_w = 64.8 \times 10^3$ and the polyethylene block was deuterated, and found that the diffraction peaks from the lamellae shifted to larger scattering angles with increasing temperature, indicating changes in the lamellar spacing.

The shifting was done by superimposing the data in the plateau region on the assumption that the plateau modulus is independent of temperature. The shift factors are plotted against temperature in *Figure 4a* and the 200–100°C region is enlarged in *Figure 4b*. The shift factors for APP and PE coincided with each other in the temperature range of 100–200°C as shown in the figures. This provides an empirical reason why the time–temperature superposition of DEP was valid. This is because DEP consists of APP and PE blocks and both blocks have the same or nearly the same shift factor, so the temperature dependences for all relaxation times in DEP are apparently characterized by only one shift factor. In *Figure 4a*, all data points seem to be fitted by the WLF equation[13]:

$$\log a_T = \frac{c_1(T - T_{\text{ref}})}{c_2 + T - T_{\text{ref}}} \qquad (3)$$

Here, T_{ref} is the reference temperature of 140°C for all samples and c_1 and c_2 are constants, in our case 3.55 and 203 K, respectively. According to the time–temperature superposition principle, the shift factor can be universally expressed by equation (3) with the same value of c_1 and c_2, regardless of the nature of the polymer provided that T_{ref} is taken as the glass transition temperature (T_g for each polymer. However, in *Figure 4*, we chose T_{ref} as 140°C for all samples independently of the differences in T_g for APP and PE. In fact T_g for APP is about 0° as shown in *Table 1* and T_g for PE must be far below this temperature range, probably below -100°C[14]. Therefore, the coincidence in the temperature dependence of the shift factor is unusual and needs interpretation. *Figure 4b* shows that in the range of 200–100°C, all data points including DEP follow the Arrhenius type relation:

$$\log a_T = \Delta H_a / RT \tag{4}$$

providing an apparent activation energy, ΔH_a, about $10\,\text{kcal mol}^{-1}$. It is well known that the WLF equation approaches Arrhenius form for temperatures in excess of $\approx T_g + 100°\text{C}$. Although equation (4) is empirical, the value of ΔH_a has been related to the molar volume of the side chain and chain stiffness[15]. In terms of the Rouse theory[13], we may consider that both APP and DEP chains have nearly the same monomeric friction coefficient which characterizes rheological properties in the terminal zone. This is not surprising because APP and PE are polyolefins which have very similar chemical structures and there are no bulky side chains.

Temperature dependence of moduli for DEP and DEP/TCB solutions

Figure 5 shows the frequency dependence of G' and G'' at 140°C for bulk DEP99 and its 50% and 15 vol% solutions in TCB. With increasing amounts of solvent in the solutions, the value of the moduli decrease and the plateau zone shifts to the higher frequency side due to the decrease in entanglement coupling from swelling by the solvent. The frequency dependence of the moduli of the solutions seems parallel to the bulk. This indicates that microphase separation is still present at these concentrations. *Figure 6* shows the temperature dependence of moduli for DEP99 and the solutions. If there were an ODT, one would observe a drop of about one decade in the moduli at this frequency[2,6]. However, all data points for each sample decrease smoothly with increasing temperature. This feature confirms microphase separation in all solutions in this temperature range.

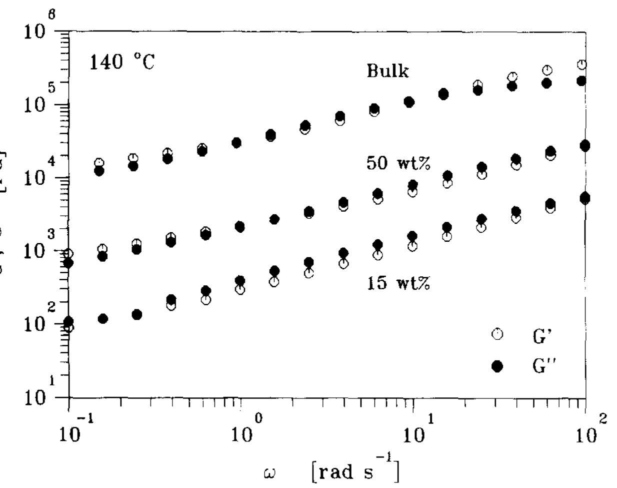

Figure 5 Comparison of frequency dependence of the bulk and solutions for DEP99 at 140°C

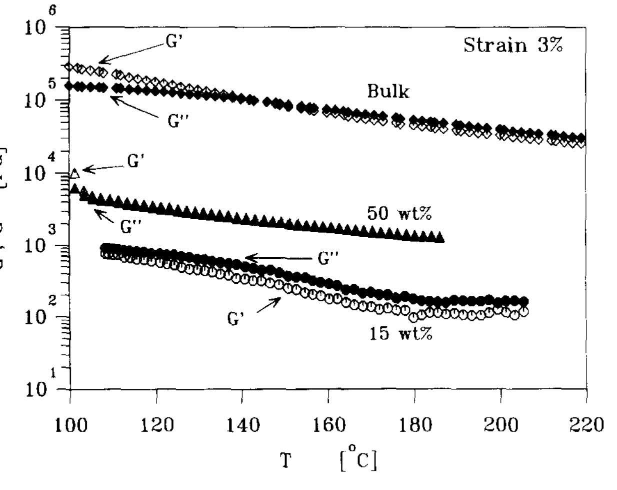

Figure 6 Temperature dependence of G' and G'' at a strain amplitude of 3% and a single frequency of $10\,\text{rad s}^{-1}$ while heating

Estimation of the order of the interaction parameter

The fact that the 15% solution of DEP99 in TCB was found to be heterogeneous by its rheological behaviour allows us to put a lower bound on the level of the interactions between PE and APP. For a non-preferential solvent, we can write the following expression for the effective interaction parameter between the two blocks as a function of the volume fraction of block polymer, ϕ_p:

$$\chi_{\text{sol}}(\phi_p) = \phi_p \chi \tag{5}$$

In order to remove any ambiguity that can arise from the definition of the repeat unit or the monomer volume (which is different for the two blocks under consideration here), we prefer to discuss this in terms of the interaction energy density, B, which is defined as

$$B = \left(\frac{\chi}{\nu}\right) RT \tag{6}$$

where ν is the reference volume that was used in the original definition of χ from the Flory–Huggins–Staverman expression for the free energy of mixing. In general, ν is taken as $\sqrt{\nu_1 \nu_2}$, the square root of the product of the molar volumes of the two monomers, but we emphasize that B does not depend on the definition of ν, although χ does. By equation (1), the critical value of χ for microphase separation of a diblock is given by

$$\chi_c = \frac{10.5}{N} \tag{7}$$

so the corresponding critical value of the interaction energy density, B_c, is given by

$$\begin{aligned} B_c &= \frac{10.5}{N\nu} RT \\ &= \frac{10.5}{M} \rho RT \end{aligned} \tag{8}$$

For DEP99, we expect a density of $0.795\,\text{g cm}^{-3}$ at 140°C (using a thermal expansion coefficient of $7.2 \times 10^{-4}\,\text{K}^{-1}$, which is typical of polyolefins[16]), so at this temperature $B_c = 0.289\,\text{MPa}$. The fact that the 15% solution was heterogeneous means that $B(\phi_p = 1) > B_c/0.15$, so for PE and APP a lower limit for B is 1.93 MPa.

Now the interaction energy density (or interaction parameter) for PE and APP has not been measured directly from their blends, since one would need to use very low molecular weights (in the order of 3000, according to the results here)[17]. However, Lohse *et al.*[18] have recently published a set of solubility parameters for model polyolefins, which is based on SANS measurements of the miscibility of a large number of blends. This compilation includes both APP (hydrogenated poly(2-methyl-1,3 pentadiene)) and 'PE' (hydrogenated polybutadiene containing 8% vinyl groups, just like the block under consideration here). Using those values we derive a value for B of 1.51 MPa at 140°C. This is close to, but clearly less than, the lower limit given above from the DEP99 solutions.

Before we discuss the possible reasons for this discrepancy, it will be useful to consider similar results from blends and block copolymers of other polyolefins. Lohse *et al.*[19] have considered the system of APP and PEP, hydrogenated polyisoprene. The interaction parameter was estimated by finding the critical molecular weights for phase separation in both the blends and block polymers, as determined by thermal measurements at 27°C. The results from both the blends and the block copolymers agreed well, giving an interaction density B of 0.0981 MPa. This agrees well with direct measurements by SANS of $B = 0.103$ MPa[17]. However, the use of the solubility parameters list, derived from blends of APP and PEP with other polymers, does not agree, giving a B of 0.490 MPa at 27°C. This difference was attributed to special mixing effects in the PEP/APP blends. A second system with which we can compare the PE/APP results is that of PE and PEE, poly(ethyl ethylene) (hydrogenated polybutadiene with 100% vinyl groups). Again, there is no direct measure from their blends, but the solubility parameter method gives a value of $B = 2.62$ MPa at 100°C. Data on block copolymer ODTs from Bates *et al.*[20] gives a value of 1.32 MPa. Again, the directly measured value is substantially smaller than the estimated one, indicating that there are some special mixing effects operating in these mixtures.

Returning to a consideration of the PE–APP block polymer results, there are several possible explanations for the discrepancy between the estimate from solubility parameters and the rheological results. First, there could be some special mixing effects that increase the value of B over that expected from the solubility parameters. This would not have to be very large, and so there could be a number of possible causes for this, such as some sort of packing effect. Secondly, it may be that equation (1) does not hold exactly for block polymers. However, it has been well confirmed before, as mentioned above, so we do not hold this to be likely. Third, it could be that the rheological determination of ODT is not precise, and that in fact the 15% solution was in a homogeneous state, although near the ODT. However, the utility of this method has been well established[20], and we reject this as well. Finally, it is possible that TCB is a preferential solvent for either APP or PE, which would invalidate equation (5). This is also unlikely, considering the chemical similarities of APP and PE. Thus, we hold that the first explanation is the one which holds, and so we will be pursuing SANS measurements of the PE–APP interaction parameter directly, on low molecular weight blends, and by the study of DEP block polymers of lower molecular weight.

CONCLUSIONS

Rheological studies on DEP99 showed that superposition time temperature principle appeared to be valid within experimental error, and that the dynamic storage and loss responses at low reduced frequencies exhibited a limiting frequency dependence of $G' \approx G'' \approx \omega^{0.5}$. This terminal zone behaviour for DEP99 is consistent with the presence of a lamellar structure in the melt state. A solution diluted to 15 vol% of DEP99 showed inhomogeneity in the temperature range of 100–200°C. The result indicates that strong microphase segregation occurred in DEP99.

ACKNOWLEDGEMENTS

We thank Mr E. Habeeb and Mr R. Krishnamoorti for their assistance with hydrogenation. We also acknowledge Prof. M. Muthukumar and Dr L. J. Fetters for helpful discussions. K. S. extends appreciation to Kanebo Ltd. for providing him with the opportunity to work on this project. Acknowledgement is made to the UMass Material Research Laboratory, funded by the National Foundation for support through the use of the central facilities.

REFERENCES

1 Balsara, N. P., Perahia, D., Safinya, C. R., Tirrell, M. and Lodge, T. P. *Macromolecules*, 1992, **25**, 3896

2 Rosedale, J. H. and Bates, F. S. *Macromolecules* 1990, **23**, 2329

3 Bates, F. S. *Macromolecules* 1984, **17**, 2607

4 Leibler, L. *Macromolecules* 1980, **13**, 1602

5 Herman, D. S., Kinning, D. J., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1987, **20**, 2940

6 Agarwal, S. (Ed.) 'Block Copolymers', Plenum Press, New York, 1970

7 Hamley, I. W., Koppi, K. A., Rosedale, J. H., Bates, F. S., Almdal, K. and Mortensen, K. *Macromolecules* 1993, **26**, 5959

8 Rubinstein, R. and Obukhov, S. P. *Macromolecules* 1993, **26**, 1740

9 Sakurai, K., MacKnight, W. J., Lohse, D. J., Schulz, D. N. and Sissano, J. A. *Macromolecules* 1994, **27**, 4941

10 Xu, Z., Mays, J. W., Chen, X., Hadjichristidis, N., Schilling, F., Bair, H. E., Pearson, D. S. and Fetters, L. J. *Macromolecules* 1985, **18**, 2560

11 Raju, V. R., Rachapudy, H. and Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1223

12 Sakurai, K., MacKnight, W. J., Lohse, D. J., Schulz, D. N., Sissano, J. A., Lin, J. S. and Agamalyan, M. *Polymer* 1996, **37**, 4443

13 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn, Wiley, New York, 1980, p. 374

14 Krigas, T. M., Carella, J. M., Struglinski, M. J., Crist, B., Graessley, W. W. and Schilling, F. C. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 509

15 Porter, R. S., Johnson, J. F. *J. Polym. Sci, C* 1966, **15**, 365, 373

16 Hattam, P., Gauntlett, S., Mays, J. W., Hadjichristidis, N., Young, R. N. and Fetters, L. J. *Macromolecules* 1991, **24**, 6199

17 Wignall, G. D., Child, H. R. and Samuels, R. J. *Polymer* 1982, **23**, 957

18 Lohse, D. J., Balsara, N. P., Fetters, L. J., Schulz, D. N., Sissano, J. A., Graessley, W. W. and Krishnamoorti, R. in 'New Advances in Polyolefins' (Ed. T. C. Chung), Plenum Press, New York, 1993, p. 175

19 Lohse, D. J., Fetters, L. J., Doyle, M. J., Wang, H-C. and Kow, C. *Macromolecules* 1993 **26**, 3444

20 Bates, F. S., Schulz, M. F., Rosedale, J. H and Almdal, K. *Macromolecules* 1992, **25**, 5547