

Rheological properties and morphology of binary blends of a longitudinal polymer liquid crystal with engineering polymers

Witold Brostow*

Departments of Materials Science and Chemistry, University of North Texas, Denton, TX 76205-5308, USA

and Tomasz Sterzynski and Sébastien Triouleyre

Ecole Européenne de Chimie des Polymères et des Matériaux, Université Louis Pasteur, 4 rue Boussingault, F-67000 Strasbourg, France

(Received 5 June 1994; revised 16 August 1995)

Earlier work on mechanical properties and their relation to phase diagrams is complemented here by rheological and further morphological studies using an optical microscope and polarizing light, for the system studied previously and also for three other binary blend systems. The polymer liquid crystal (PLC) is the same in all, PET/0.6PHB, where PET = poly(ethylene terephthalate), PHB = *p*-hydroxybenzoic acid and 0.6 = the mole fraction of PHB in the copolymer. The engineering polymers (EPs) used are, in turn, bisphenol-A-polycarbonate (PC), poly(butylene terephthalate) (PBT), isotactic polypropylene (PP) and poly(vinylidene fluoride) (PVDF). Blends of concentration up to 20 wt% PET/0.6PHB were studied. In all four binary systems and for all shear rates, the addition of PET/0.6PHB to an EP results in a lowering of the melt viscosity (η), down to approximately 30% of the value for the respective pure EP. The results are explained in terms of the Wissbrun model of PLC melts; the mechanism of the viscosity lowering is different from that in incompatible blends of flexible polymers. With the exception of PC + PET/0.6PHB blends, a shear rate dependence of the viscosity modification by the PLC is also observed. This difference can be explained by the miscibility of PC with PHB in the PLC as reported earlier, while the remaining three EPs are immiscible with the PLC. The concentration $\theta_{LC \text{ limit}}$ at which liquid crystal (LC)-rich islands are formed in the LC-poor matrix is between 15 and 20 wt% PLC in the systems studied. An equation for blend viscosity proposed by Borisenkova *et al.* has been generalized to the form $\ln(\eta_{\text{blend}}/\eta_{\text{matrix}}) = a_0 + a_1 \ln(\eta_{\text{matrix}}/\eta_{\text{PLC}}) + a_2 \ln^2(\eta_{\text{matrix}}/\eta_{\text{PLC}})$, where a_0 , a_1 and a_2 are parameters for a given class of blends; the type of EP and the shear rate are implicit variables which define $\eta_{\text{matrix}}/\eta_{\text{PLC}}$. The master curve corresponding to that equation exists only for $\theta \geq \theta_{LC \text{ limit}}$. Copyright © 1996 Elsevier Science Ltd.

(Keywords: binary blends; polymer liquid crystal; engineering polymers; rheology; morphology; melt viscosity)

INTRODUCTION

Polymer liquid crystals (PLCs) constitute an important group of polymers with advantageous properties, particularly in applications in which high temperatures, high resistance to deformation and low thermal expansivity are required. In spite of these advantages, widespread use of PLCs is still limited because of their high prices. Therefore, as discussed in the literature (including our companion paper¹ and in some detail in reviews by one of us^{2–4}), blends of PLCs with engineering polymers (EPs) are being made. Blending PLCs with thermoplastic EPs makes possible the creation of engineering materials with relatively low prices and improved properties compared with their pure EP components.

Thermotropic PLCs can be processed using standard techniques for thermoplastics such as injection moulding. In many cases PLCs are low viscosity materials in

comparison with EPs, so processing is even easier. However, there are various unexpected pitfalls, and there is no clear picture of rheological behaviour of PLCs. A few examples will illustrate the prevailing situation. PLC chains exhibit semiflexibility (also known as semiridigity). The excluded volume effect is strong, even in athermal solutions in the isotropic phase, as already recognised by Onsager⁵ in 1949 in the first theory of such systems. However, modern theories of isotropic phases of liquid crystal (LC)-forming systems only in part survive confrontation with experimental results, as performed by DeLong and Russo⁶. When cooling some poly(ester imide)s from the isotropic into the nematic state, de Abajo and co-workers⁷ found viscosities higher than during the preceding heating operation. By contrast, cooling LC polyurethanes resulted in viscosities four orders of magnitude lower than those during the heating process⁸. Kannan, Kornfield, Schwenk and Boeffel (KKSB)^{9,10} found fairly strong coupling between the flexible backbones and LC side chains in PLC

* To whom correspondence should be addressed

combs—this in contrast to results of earlier investigators. These results pertain to pure PLCs, while PLC-containing blends with which we are now dealing are necessarily even more complicated. Borisenkova, Kulichikhin and Platé (BKP)¹¹ have developed a correlation for the viscosities of PLC blends in the melt region; they realized that their formula has a limited application range, but they were unable to define that range.

Clearly, more concepts (and more data) are needed to improve our understanding of the rheology of thermotropic PLC melts. The present work deals with the rheological properties and morphology of binary blends of a PLC with four commercially used EPs. One of the four systems is the same as that studied using mechanical and thermophysical techniques in our companion paper¹. Thus, the PLC used is a longitudinal one, with LC sequences in the backbone along the main-chain direction^{2–4}, the remaining sequences being flexible; this should provide a relatively firm basis for the interpretations. Moreover, we had at our disposal the full phase diagram for the copolymers to which our PLC belongs¹². First we review concepts and results pertinent to the task at hand. Then we define the systems studied, report and discuss the results pertaining to rheology and morphology, perform certain calculations on the basis of the rheological data and finally make some general comments.

BACKGROUND

A theory of the rheological behaviour of pure PLC melts has been developed by Wissbrun¹³. The melt is assumed to consist of a space-filling system of domains. At rest, the minimum of the energy U of the system is achieved when the directors in the planes of contact are parallel to each other. Under shear, domains slide over each other; the domain size decreases because of the application of the stress. The model predicts shear sensitivity, including shear thinning, and has found experimental confirmation¹⁴.

The systems we are working with, however, contain relatively rigid LC domains in a flexible matrix. Since the two types of sequences are connected by primary chemical bonds, then each predominantly flexible LC-poor phase contains a certain number of LC sequences while each LC-rich phase, called an island¹⁵, necessarily contains some flexible sequences. The existence of two phases in thermotropic PLCs was established in 1980 by Menczel and Wunderlich¹⁶, who, using differential scanning calorimetry (d.s.c.), observed two glass transition temperatures; the result was subsequently confirmed by a more extensive study¹⁷. Morphology studies by Crevecoeur and Groeninckx^{18,19} showed the islands and the changes of their shapes as a function of the processing procedure: injection moulding, extrusion or fibre spinning. The islands are similar to the domains of Wissbrun, and we have to see whether his theory of neat PLCs can be applied to the islands.

Let us denote by θ the concentration of the LC constituent. This is an overall concentration, for instance molar; then in pure PLC copolymers $\theta = x$, where x is the mole fraction of the LC sequences in the chains. In PLC + EP blends we thus have $\theta < x$. It is important for our subsequent considerations to note that the islands are formed only above a certain limiting θ value that will

be called $\theta_{\text{LC limit}}$. This limit has been discussed previously²⁰; it has also been shown in phase diagrams determined experimentally in refs 1 and 12.

As already noted in the companion paper¹, there exists a statistical mechanical theory of PLCs developed by Flory and co-workers^{21–24}, amplified by Matheson^{24,25} and then also by us^{19,26,27}. In a study of ternary systems of the type PLC + flexible polymer + solvent, it has been found that solvent molecules are structured into channels by the LC sequences in PLCs, with perhaps unwilling flexible sequences participating in the channelling²⁶. It remains to be seen to what extent the LC sequences produce comparable channelling of the flexible ones in the melts.

BKP¹¹ looked for a way to generalize the behaviour of PLC-containing melts. They have proposed a formula which, in obvious notation, can be written as

$$\ln(\eta_{\text{blend}}/\eta_{\text{matrix}}) = a'_0 + a'_1 \ln(\eta_{\text{m}}/\eta_{\text{PLC}}) \quad (1)$$

where η is the melt viscosity while a'_0 and a'_1 are constants. BKP have shown that equation (1) applies in a number of cases, but (as already noted in the Introduction) they were unable to define the range of application of their formula. At the end of their paper they make a somewhat confusing statement that 'the suggested generalization refers to 30% content of the disperse phase, but it can also be realized at lesser concentrations'.

Heino *et al.*²⁸ studied blends of five different grades of polypropylene (PP) with two PLCs, one our PET/0.6PHB and the other known under the tradename Vectra A950, in each case for the PLC concentration of 20 wt%. The morphologies of blends they produced by using several kinds of mixing ratios of the components and found that high $\eta_{\text{PLC}}/\eta_{\text{matrix}}$ ratios resulted in the formation of spherical islands rather than fibrils. Moreover, Heino *et al.* found that PLC addition generally resulted in viscosity decreases compared with the pure components. However, other investigations—particularly by cone-plate rheometry of blends containing up to 35% of a longitudinal PLC (two studied in ref. 29 and one in ref. 30)—showed that shearing flow does not lead to a decrease of the viscosity. Even at low shear rates certain increases of η have been observed.

We already commented in the Introduction on the complex rheological behaviour of PLCs and their blends. We shall now mentioned briefly some other experimental studies which might be helpful in our quest for the understanding of PLC rheology. La Mantia *et al.*³¹ found large variations of the viscosity η with temperature T , especially around the solid-nematic transition temperature, as well as high values of relaxation times in the molten state. Geiger³² as well as others^{31,33} showed that the deformation history plays an important role in the rheological properties and structures of PLCs. In particular, a pre-sheared polymer exhibited lower η values than an unsheared material. Injection moulding or extrusion results in the formation of highly oriented structures; elongational as well as shearing flows contribute to the orientation. The elongational flow in the advancing melt front during injection moulding as well as an expanding flow in the vicinity of the mould gate cause an orientation in the flow direction. This is in contrast to shear flow, in which at a certain distance from

Table 1 Properties of thermoplastic engineering polymers (ρ = density at 25°C; MFI = melt flow index; σ_y = stress at yield; E = modulus of elasticity; ϵ_b = elongation at break; T_m = melting temperature; η = viscosity at the strain rate $\dot{\gamma} = 31.5 \text{ s}^{-1}$, each time at the temperature defined in square brackets)

Engineering polymer	ρ (g cm^{-3})	MFI ($\text{g}/10 \text{ min}$)	σ_y (J cm^{-3})	E (J cm^{-3})	ϵ_b (%)	T_m (°C)	η ($\text{s } \mu\text{J cm}^{-3}$)
Polycarbonate (Macrolon 2800)	1.21	7 to 10	65	2300	110	250	385 [290°C]
PVDF (Solef 1008)	1.78	6	50	1800	50	190	829 [270°C]
PBT (Vestodur 3001 nf)	1.31	10	55	2600	>50	232	380 [250°C]
iPP (Neste VB65)		6.5	35	1760	470	167	648 [230°C]

Table 2 Parameters of blending

Blend	Barrel temperatures (°C)	Screw rotation speed (rev min^{-1})	Residence time (min)
PC + PLC	230–260–270	40	2
PLC + PVDF	180–230–250	45	2
PLC + PBT	180–235–240	35	2
PLC + PP	210–220–230	55	2

the cold cavity wall a different orientation is obtained, sometimes accompanied by the formation of a layer structure. In extrusion, as a result of the converging and diverging flows at the die entry or as a result of the extrudate pull, usually elongational flow and the corresponding orientation may be observed. Kenig³⁴ found in extrusion that the extent of orientation induced by the shear flow depends on the length of the die. Ziabicki³⁵ studied the effect of the nematic order on the orientation, stress field characteristics, relaxation times and crystallization by spinning of polymer fibres. He concluded that particularly important in this case is the relaxation time for PLC molecules, which is usually several times longer than for flexible polymer chains. This results not only in the formation of highly oriented structures, but also in the preservation of such structures at long times. We have argued before^{1,3,12} how important some non-equilibrium structures with high longevity are in PLCs. Lowering of the viscosity of an EP by the addition of a PLC was reported by a number of investigators, including Acierno and his colleagues³⁶, Kyu and Zhuang³⁷ and Aiji and Gignac³⁸.

The rheology of PLC-containing blends is necessarily affected by the miscibility or compatibility of the components. There are no general rules here either. For example, Kyu and Zhuang³⁷ have found that our PET/0.6PHB is totally immiscible with polystyrene (PS). By contrast, they infer that the same PLC is miscible with polycarbonate (PC), while a detailed study in the companion paper¹ shows that actually PC and PHB are miscible in the solid phases, but PC and PET are not. We assume that miscibility means that two or more components can be found together in an equilibrium phase, while compatibility means that the components 'tolerate' each other without necessarily forming a stable equilibrium phase. There is no general agreement on the terminology in this area, and other authors might use other definitions of miscibility and compatibility. We have just pointed out above the role of long-living but essentially non-equilibrium phases, complicating the situation even further.

EXPERIMENTAL

Systems studied

As a polymer liquid crystal we have used PET/0.6PHB produced by Unitika Ltd., Kyoto, Japan (LC-3000), the same longitudinal PLC that was studied in the companion paper¹ as well as in earlier work^{12,15,39–41}. Its melting point is $T_m = 199^\circ\text{C}$; its viscosities determined as described below at the temperatures 250, 270 and 290°C are respectively 165.7, 50.4, and 37.7 $\text{s } \mu\text{J cm}^{-3}$.

Four different thermoplastic engineering polymers were used in our investigations: polycarbonate (PC), Makrolon 2800 produced by Bayer AG; poly(vinylidene fluoride) (PVDF), Solef 1008 produced by Solvay; poly(butylene terephthalate) (PBT), Vestodur 3001 produced by Hüls AG; and isotactic polypropylene (iPP, PP), VB65 produced by Neste Oy. *Table 1* presents pertinent data for these polymers.

Each of the four EPs was blended with PET/0.6PHB in the following concentrations: 5, 10, 15 and 20 wt% PLC. For comparison purposes, pure EPs as well as pure PET/0.6PHB were studied as well.

Sample preparation and processing

To exclude possible degradation of the macromolecular chains by hydration, the polymers were dried in a vacuum drier before processing as follows: PET/0.6PHB for 8 h at 130°C; PC for 6 h at 125°C and PBT for 4 h at 100°C.

The blending was done using a single-screw Goettfert extruder with diameter $\varnothing = 20 \text{ mm}$ (the ratio length/diameter $L/D = 20$) and a 3 mm cylindrical die. Extruded rods were granulated using a pelletizing unit. The temperatures of the heating zones of the barrel and screw rotation speed used for the blending are listed in *Table 2*.

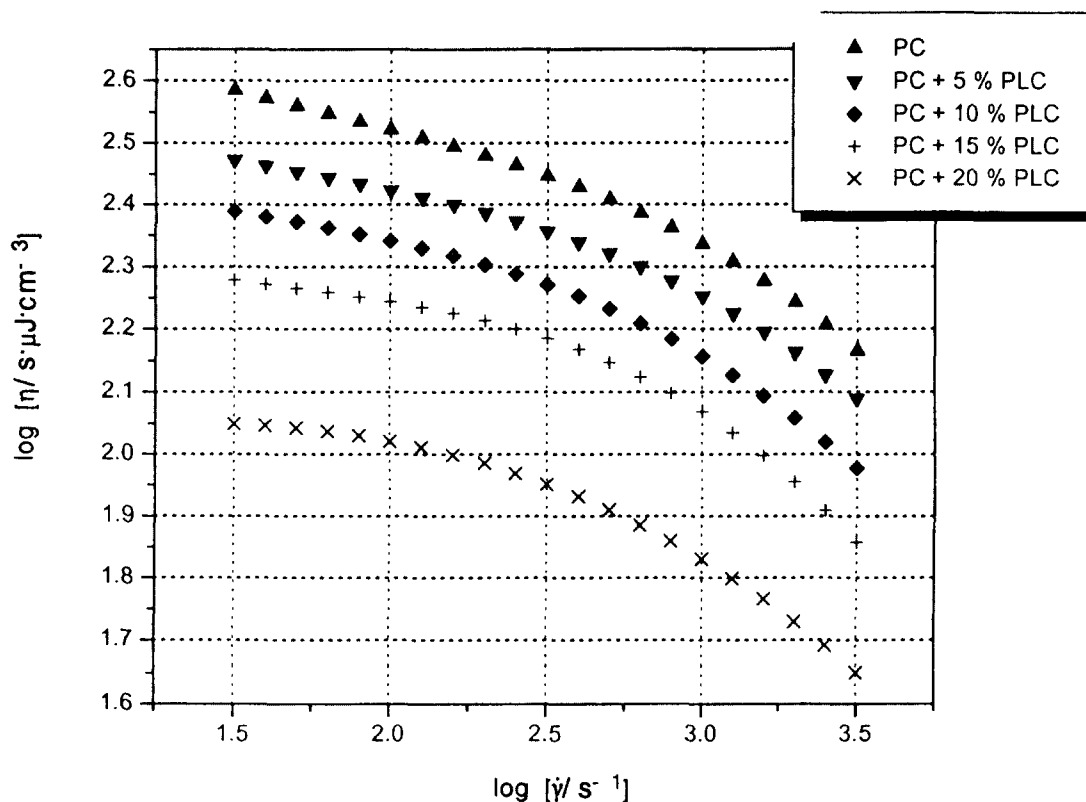
The samples used for the microscopic observations were prepared by injection moulding. This was conducted at fairly high temperatures so as to ensure processing of the material in LC phases and the formation of the LC-rich regions in a thermoplastic matrix. Pressures are given in J cm^{-3} , where $1 \text{ J cm}^{-3} = 1 \text{ MN m}^{-2} = 0.1 \text{ bar}$ exactly. The injection moulding parameters are listed in *Table 3*.

EXPERIMENTAL RESULTS ON BLEND RHEOLOGY

The elongational viscosity was measured using a Rosand Advanced Rheometer System equipped with two capillary dies of diameter 1 mm and lengths of 4 and 32 mm, respectively. The application of a two capillary system permits to take into account the standard Bagley and

Table 3 Parameters of injection moulding

Blend	Barrel temperatures (°C)	Mould temperature (°C)	Filling pressure (J cm ⁻³)	Packing pressure (J cm ⁻³)	Packing time (s)	Cooling time (s)
PC + PLC	270–280–290–300	100	130	46	10	15
PLC + PVDF	190–230–240–250	80	53	50	10	15
PLC + PBT	220–260–265–270	60	53	40	10	15
PLC + PP	170–225–230–245	20	53	27	5	15

**Figure 1** Logarithmic viscosity of blends of PC with 5, 10, 15 and 20 wt% PET/0.6PHB versus logarithmic shear rate

Rabinowitsch corrections automatically during measurements. The experimental procedure for each of the blends included 16 various piston rates in the range from 1 to 400 mm min⁻¹, allowing us to determine the viscosity of the blends in the range of shear rates between 10^{1.5} and 10⁴ s⁻¹. The viscosity measurements for the blends were performed at the following temperatures: 290°C for PC-containing blends, 270°C for those with PVDF, 250°C for those with PBT, and 230°C for PP-containing blends. Thus, viscosities were determined at least some 20 K above the respective melting temperatures T_m . The choice of the temperatures of the viscosity determination for the melts T_η is a compromise between having comparable viscosities and at the same time comparable ratios T_η/T_m . We were quite successful in this for PC and PBT, but not so for PVDF and PP. While the ratio T_η/T_m for PP is higher than that for PC and PBT, the viscosity of PP is higher than that of the two polymers just named. For PVDF we went still further above the melting point, but in spite of that the viscosity was the highest of all. The results of the viscosity determinations as a function of shear rate are presented in Figures 1 to 4. The viscosity unit used

$s \mu J cm^{-3} = s Pa = s N m^{-2} = 10.00$ poise. In the figures we use quantity calculus, as recommended by the international learned unions^{42,43}.

Inspection of the figures shows shear thinning effects for all EP + PLC pairs and at all concentrations. Moreover, the results can be divided into two groups. First, for PC + PET/0.6PHB blends, the viscosity changes depend significantly on the PLC content and less on the shear rate; in other words, the shear rate dependence of viscosity is similar for all PLC concentrations. In the second group, that is in the remaining cases, variations in the shear rate affect different blend compositions in various ways.

Consider now in some detail PC + PET/0.6PHB blends; the relative changes of the viscosity are here, quite large. For instance, addition of 5 wt% of the PLC reduces the viscosity in comparison with the pure EP by approximately 30%; 20 wt% of the PLC results in viscosity reduction of the order of 50%. We observe that all viscosity curves for the PC-containing blends are nearly parallel. That is, the lubrication effect resulting from the PLC addition is practically the same for all elongation rates. To explain this result, consult the

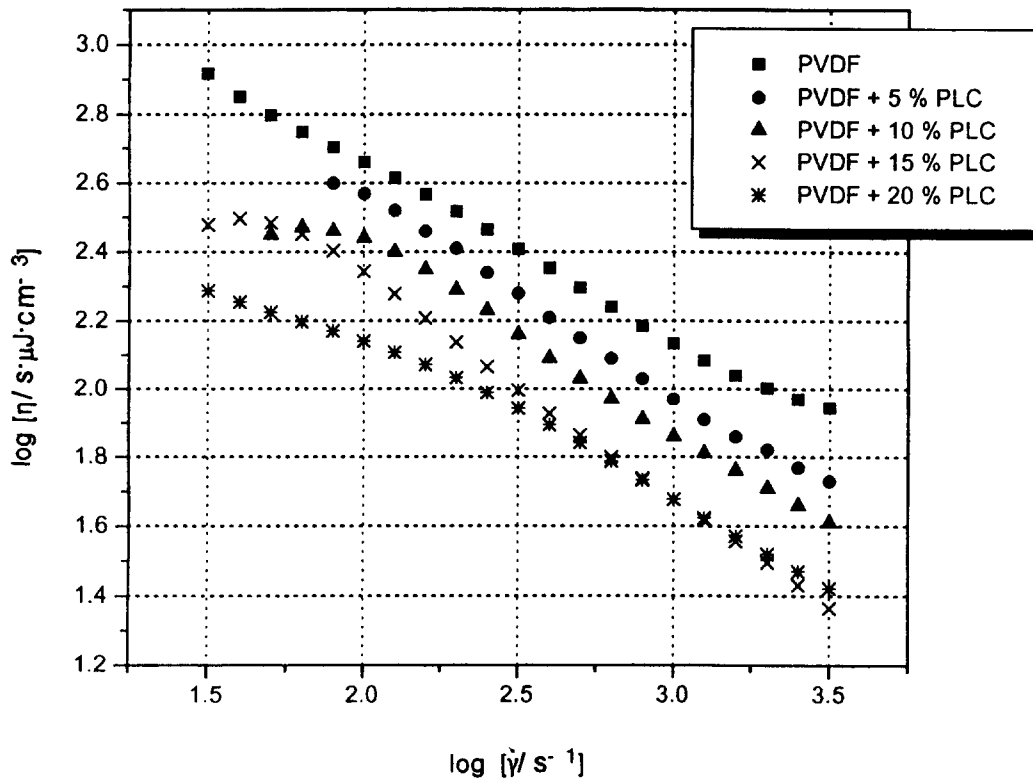


Figure 2 Logarithmic viscosity of blends of PVDF with 5, 10, 15 and 20 wt% PET/0.6PHB versus logarithmic shear rate

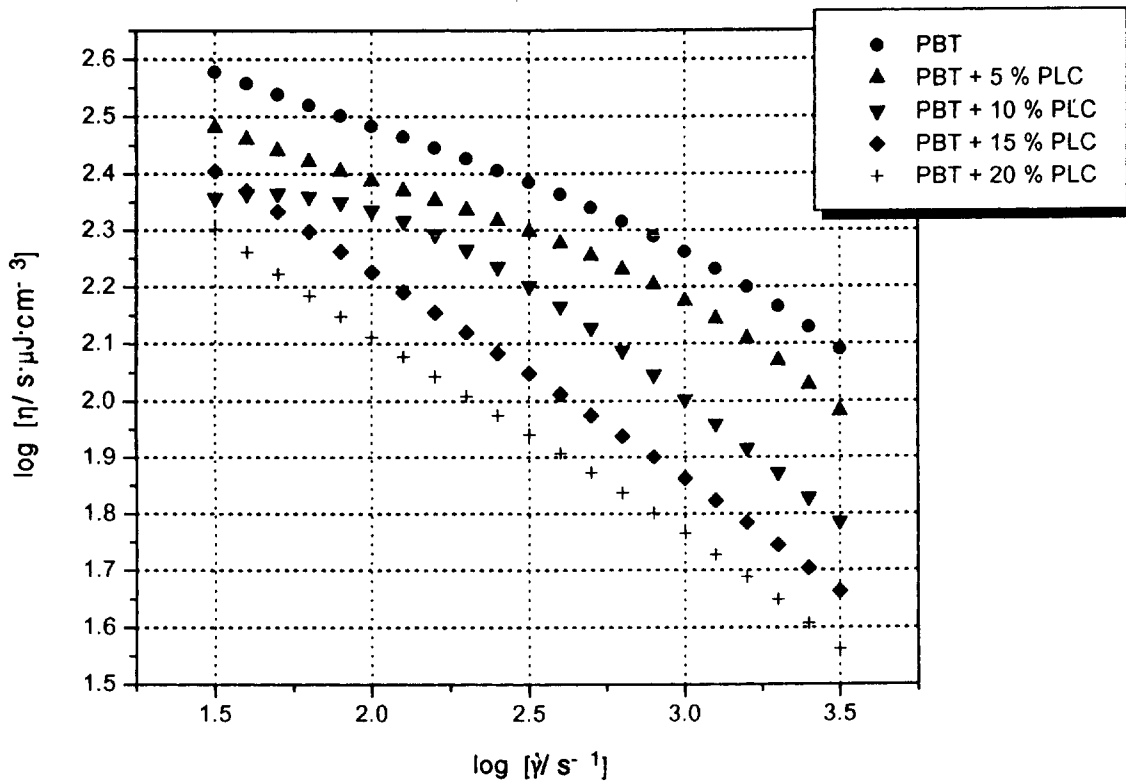


Figure 3 Logarithmic viscosity of blends of PBT with 5, 10, 15 and 20 wt% PET/0.6PHB versus logarithmic shear rate

PC + PET/0.6PHB phase diagram determined in the preceding paper¹: we are on the PC-rich side, adding a copolymer containing 60% PHB which is miscible with PC. Therefore, the shearing forces 'tackle' a largely uniform material. We have the PHB-rich islands, while

the PHB units in the flexible matrix are miscible with PC and respond approximately in unison to the shearing forces. The only constituent which does not 'cooperate' with the rest is the PET sequences in the PLC copolymer. However, even at the highest PLC concentration (20%),

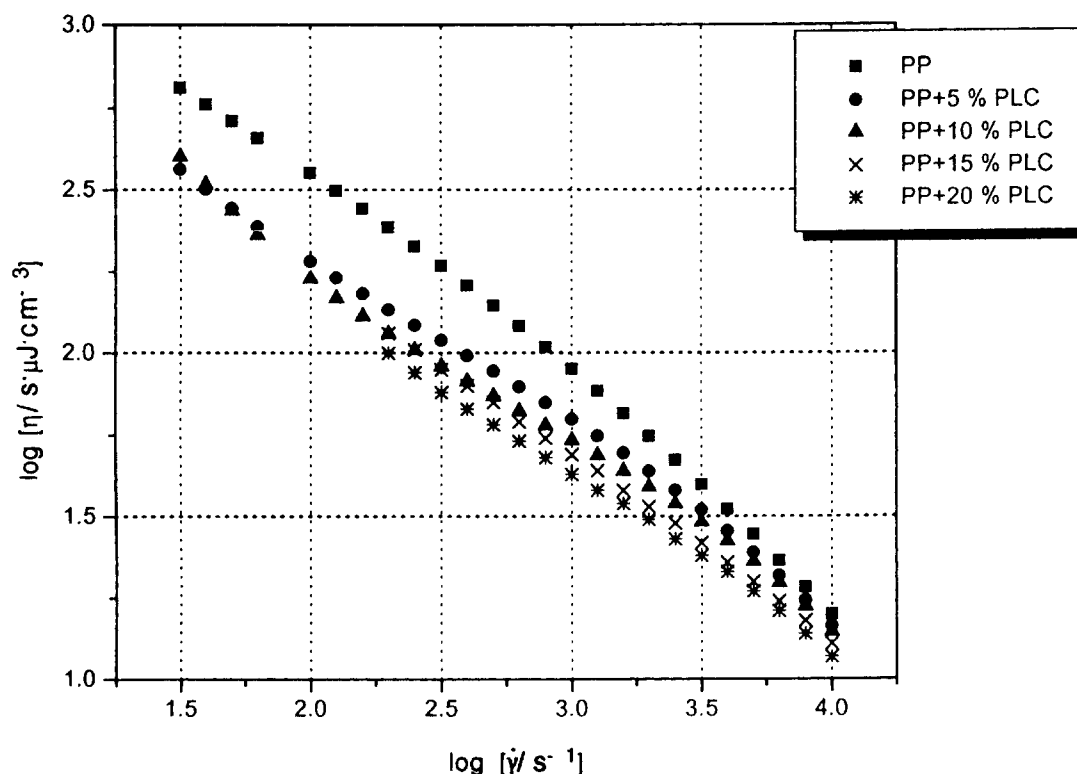


Figure 4 Logarithmic viscosity of blends of PP with 5, 10, 15 and 20 wt% PET/0.6PHB versus logarithmic shear rate

we have a molar concentration of the PET units of only 8%; the cooperative response to shear pertains to 92% of the material. Thus, while the concentration of PLC determines the viscosity values along the ordinate, the shear rate variation affects these blends in the same way. Needless to say, without having determined the phase diagram first, we would have observed this fact but there would be no explanation.

The other three binary systems investigated also exhibit considerable viscosity decreases. In contrast to PC + PET/0.6PHB blends, however, apart from viscosity lowering, a shear rate dependence of η on the PLC concentration was also observed. This can now be explained by the lack of miscibility of the PLC with the respective EPs. Immiscible constituents 'attacked' by the shearing forces do not 'cooperate' with each other, and respond individually and variously to those forces. The resulting effects depend on the specific EP + PLC pair. In PBT-containing blends the viscosity curves as a function of shear rates are divergent; in the remaining two binary systems they are convergent.

Obviously we have here two key variables: shear rate and the PLC concentration. Figures 5–8 show the PLC content dependence of the viscosity of the blends for several shear rates. For PC + PLC blends shown in Figure 5 we see that significant changes of η with concentration begin at 5 wt% PLC. In the PVDF + PLC system (Figure 6) we see lowering of η upon PLC addition, but the effects are only weakly dependent on the shear rate. In the PBT + PLC blends (Figure 7) the viscosity variation with concentration goes symbatically with the shear rate and has already begun on addition of 5% PLC. By contrast, for the PP + PLC blends we see in Figure 8 that the highest shear rate results in the weakest dependence of the viscosity on concentration. In this

system at low shear rates there are significant effects of addition of the first 5% of PLC, but only small effects afterwards.

The results observed can be explained in terms of increasing alignment of relatively rigid LC sequences during the flow. Our PLC is a longitudinal one; there are no complicating factors present such as those, for instance, in comb PLCs, where (at least in principle) decoupling of the response of the backbone and of the mesogenic units to the shearing force is possible^{9,10}. The Wissbrun model¹³ is best applicable to longitudinal PLCs, and also to the islands in blends containing them. A strong decrease in the viscosity of the PC + PLC blend between 15 and 20% PLC can be explained by island formation and by sliding of the islands over each other—as envisaged in the Wissbrun theory. An important question now is: to what extent do the LC sequences between the islands, that is in the LC-poor matrix, undergo alignment and subsequent sliding?

To answer this question, consider the results of Heino and co-workers²⁸ already mentioned above. They varied the $\eta_{\text{PLC}}/\eta_{\text{matrix}}$ ratio in PP + PLC blends, in fact in a quite large range from 2.7 down to ≈ 0.1 . The fact that polypropylenes alone have viscosities in such a wide range demonstrates the effect of molecular structure variation on properties. For high $\eta_{\text{PLC}}/\eta_{\text{matrix}}$ values Heino *et al.* found that the effects of lowering the PP viscosity by adding 20% PLC are small, what they explain by island formation; the islands are in this respect less effective than fibrils. The same investigators also noted that low $\eta_{\text{PLC}}/\eta_{\text{matrix}}$ values such as 0.1 result in a coarser morphology with less fibrils. Our own morphology studies on specimens produced by injection moulding, described below in the section on Morphology, show that the fibrils are well developed in the near-to-wall

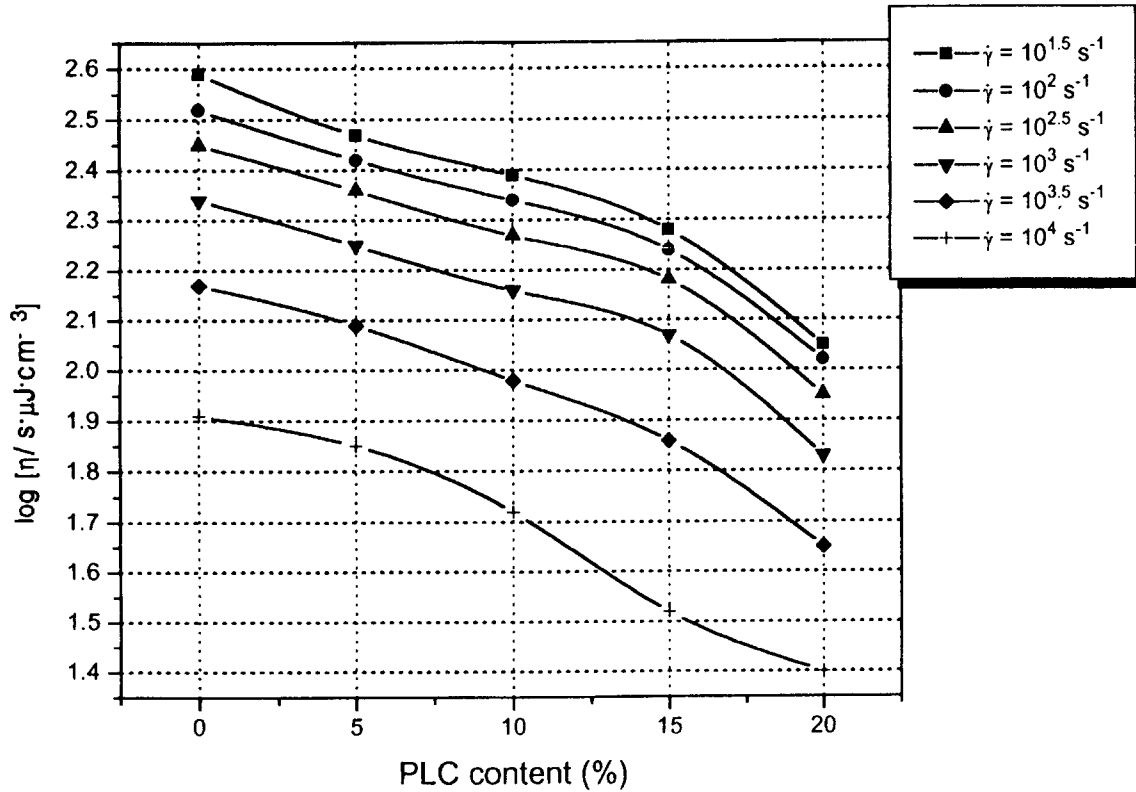


Figure 5 Logarithmic viscosity of PC + PLC blends for various shear rates versus PLC content

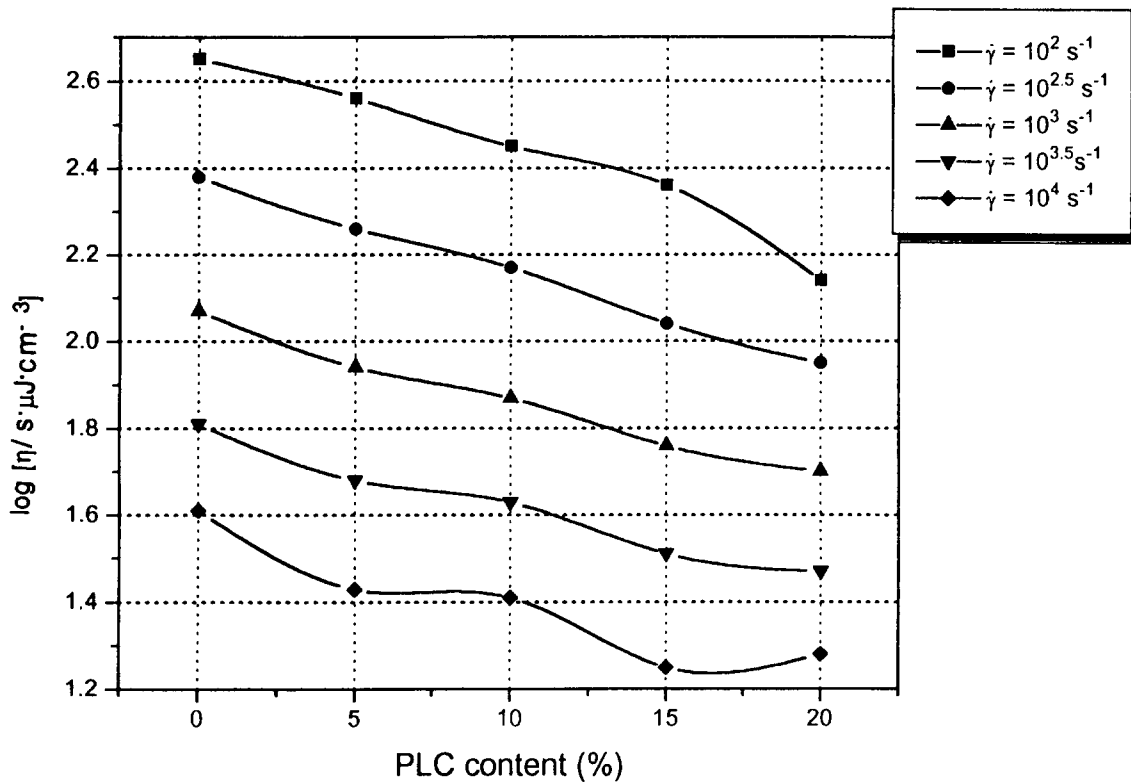


Figure 6 Logarithmic viscosity of PVDF + PLC blends for various shear rates versus PLC content

regions but much less in the middle. Looking now at our data in Table 1, we find that at the lowest shear rate of 31.5 s^{-1} the $\eta_{\text{PLC}}/\eta_{\text{matrix}}$ ratio at 250°C for PBT as the matrix is 0.437, at 270°C for PVDF the respective value is

0.061, and at 290°C for PC as the matrix the ratio is 0.098. Thus, we are at the low end of the ratio; we have found that EP viscosity lowers in all cases for PLC concentration as low as 5%. This can be explained by

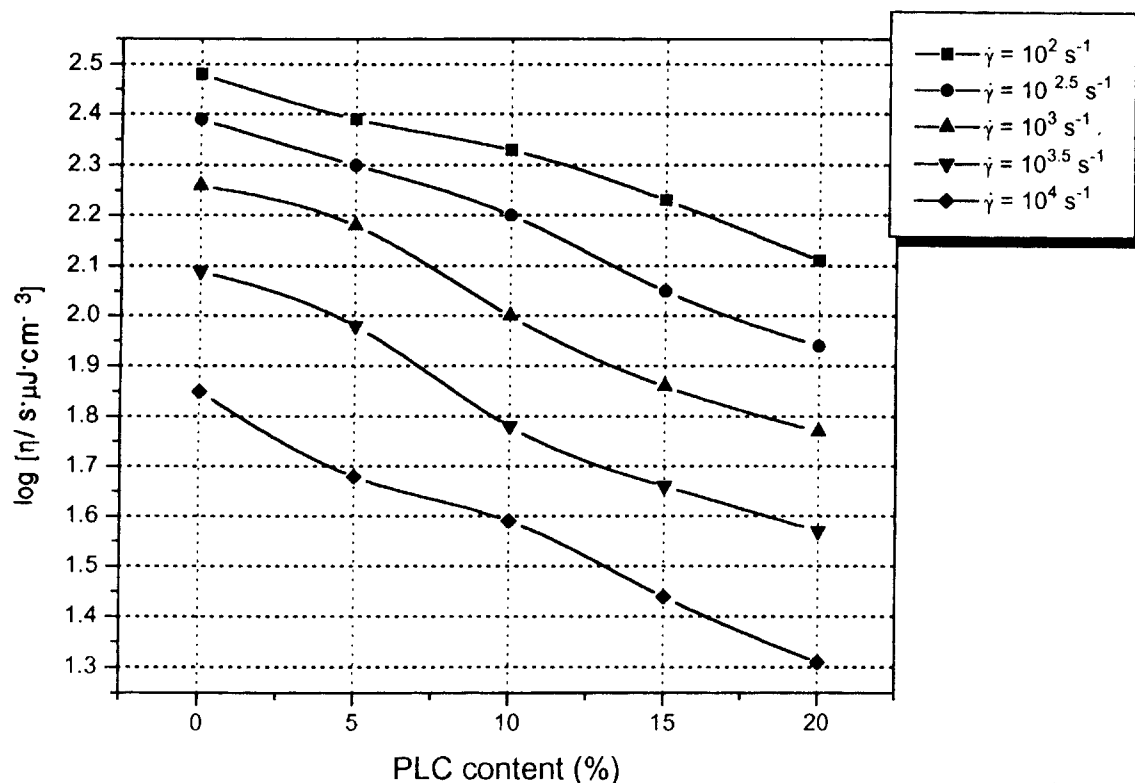


Figure 7 Logarithmic viscosity of PBT + PLC blends for various shear rates versus PLC content

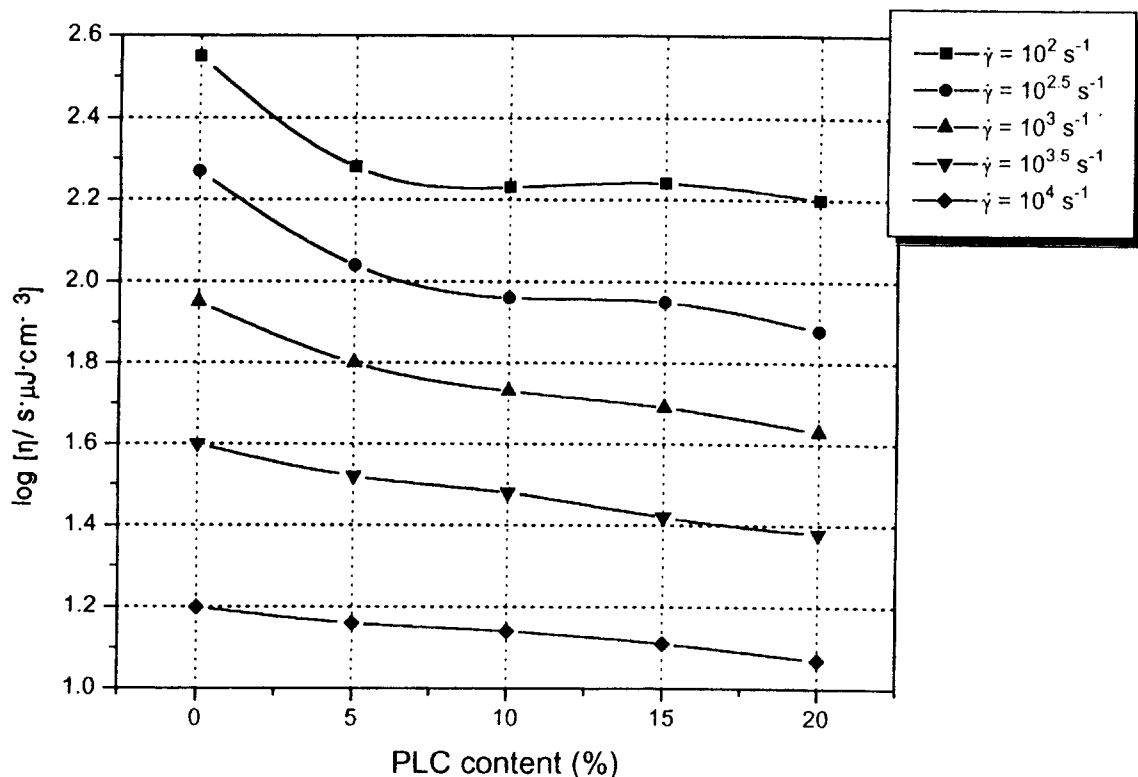


Figure 8 Logarithmic viscosity of PP + PLC blends for various shear rates versus PLC content

assuming that the process of alignment and sliding of LC sequences occurs also in the LC-poor matrix—necessarily to a lower extent than in the islands, but aided if the EP is miscible with the LC component. Thus, the semiflexibility of LC sequences and the resulting

structure ordering and anisotropy are important here. We recall the channelling effect predicted on the basis of the Flory statistical mechanical theory of PLC-containing systems²⁶.

In the Introduction we noted the contradictory results

reported in the literature on rheological behaviour of PLCs. We believe that the differences in behaviour can be traced to differences in the molecular architecture, in particular when the PLCs being compared belong to different classes of molecular structures²⁻⁴. de Abajo and co-workers⁷ pointed out that there was only a difference in the $-\text{COO}-$ group orientation between the two polymers they investigated, one of which was liquid crystalline while the other was not.

Having said this, let us try to see whether some common features do not exist after all. KKS¹⁰ pointed out that MLCs retain their alignment after the removal of a magnetic field. PLCs subjected to oscillating shear fields also align, but the orientation acquired is preserved only in part after the removal of the field. KKS¹⁰ explained this by the fact that in polymers certain structures existed before shear imposition, they were distorted during flow, and then various levels of structure relaxed on various time scales. Their conclusion agrees with our analysis of the hierarchical character of PLC structures⁴⁰. KKS¹⁰ studied combs, we are studying longitudinal PLCs. If any generalization is possible, then it might be this: shear flow destroys existing structures as well as builds new ones. Which of these effects prevails? From the preceding discussion we infer that this depends first on the class to which a given PLC belongs, and then possibly also on fine details of the molecular structures. This might well be the reason why the models of thermodynamic and dynamic behaviour of semiflexible polymers investigated by DeLong and Russo⁶ work for certain systems, but are not applicable to some other polymers.

We notice here the difference between our EP + PLC blends and the more frequent EP + EP blends. In the latter the phenomena of shear thinning and viscosity

lowering caused by the addition of a second component are usually explained in terms of incompatibility of the components. Thus η lowering, so advantageous in processing, conspires against the improvement of mechanical properties by blending. In PLC-containing blends we have 'the best of both worlds'. We have explained the viscosity lowering and shear thinning by sliding of the Wissbrun domains (our islands or fibrils); incompatibility of the blend constituents—or lack of it—is not required. Since our blend constituents are compatible (or even miscible is the case of PC + PHB), addition of a PLC to an EP results in viscosity lowering in the melts and simultaneously in improvement of the mechanical properties of the solids. As far as mechanical behaviour is concerned, the semiflexible LC sequences act similarly to short fibres in solid heterogeneous composites.

MASTER CURVES FOR BLEND VISCOSITY

As suggested by BKP¹¹, we have plotted the blend viscosity normalized with respect to the viscosity of the EP thermoplastic matrix, i.e. $\ln(\eta_{\text{blend}}/\eta_{\text{matrix}})$, as a function of the matrix viscosity normalized by the viscosity of the LC dispersed phase, $\ln(\eta_{\text{matrix}}/\eta_{\text{PLC}})$. The results are shown in Figures 9–11, respectively for blends with 10, 15 and 20 wt% of the PLC. Different points for the same EP + PLC pair correspond to different shear rates. For all our four systems

$$\eta_{\text{PLC}} < \eta_{\text{blend}} < \eta_{\text{matrix}} \quad (2)$$

Therefore

$$\ln(\eta_{\text{blend}}/\eta_{\text{matrix}}) < 0 \quad \text{while} \quad \ln(\eta_{\text{matrix}}/\eta_{\text{PLC}}) > 0 \quad (3)$$

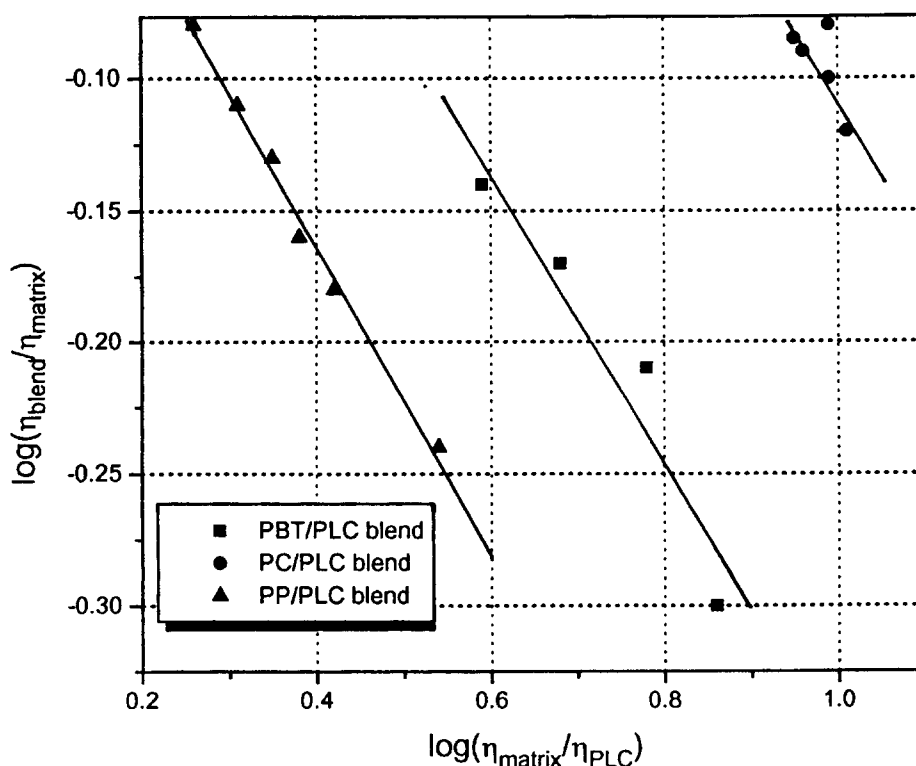


Figure 9 Logarithmic viscosity of blends with 10 wt% PLC normalized by the matrix viscosity versus logarithmic viscosity of the matrix normalized by the PLC viscosity

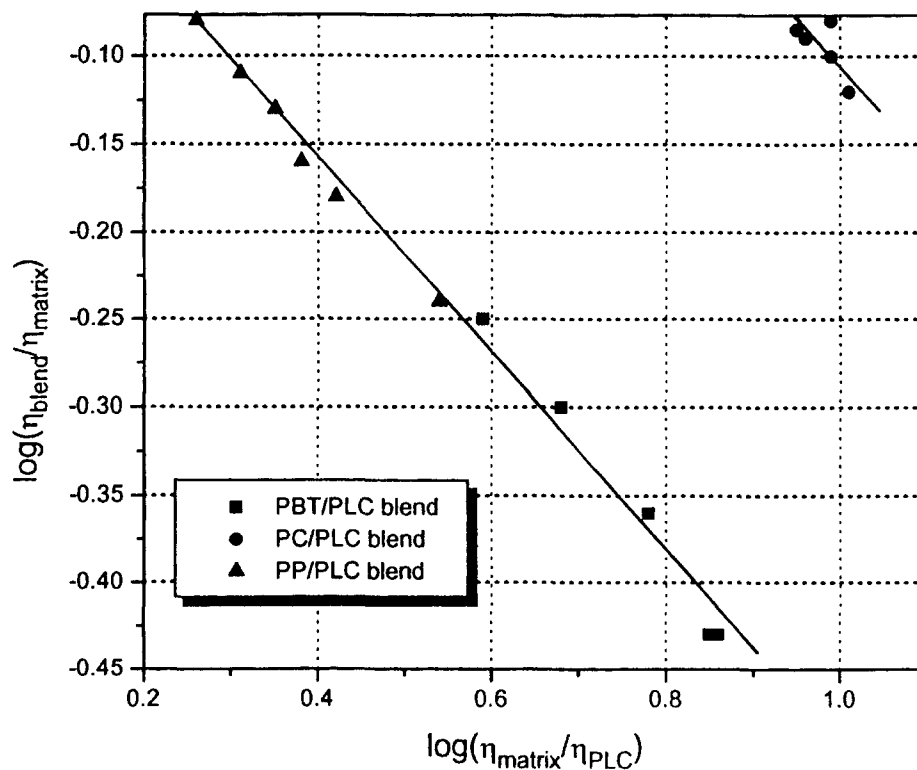


Figure 10 Logarithmic viscosity of blends with 15 wt% PLC normalized by the matrix viscosity versus logarithmic viscosity of the matrix normalized by the PLC viscosity

Normalised viscosity for the blends with 20 wt% of the PLC

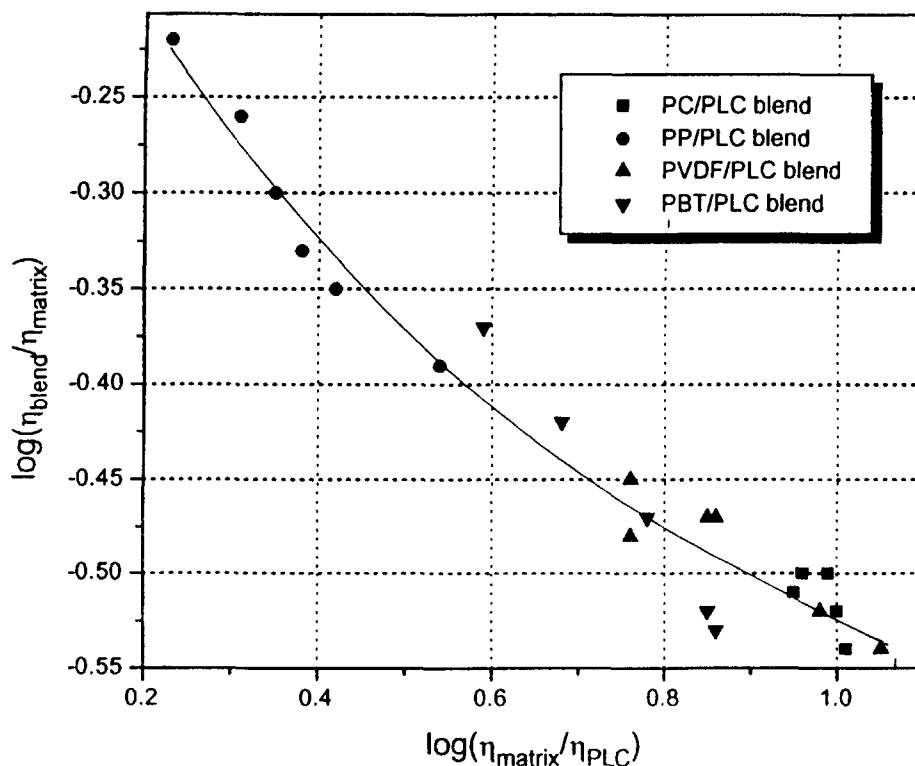


Figure 11 Logarithmic viscosity of blends with 20 wt% PLC normalized by the matrix viscosity versus logarithmic viscosity of the matrix normalized by the PLC viscosity

It may be seen in *Figure 9* for 10 wt% PLC that the plots in such reduced coordinates are approximately linear but each binary system forms a separate curve. At 15% PLC (*Figure 10*) two systems, those containing PBT and PP, form a single curve. For blends with 20 wt% PLC, experimental points for all four binary systems coalesce into a single somewhat concave curve. That is, we confirm the supposition of BKP about the existence of a master curve but only above a certain threshold of PLC concentration, and that threshold depends on the components present. Contrary to their hypothesis, there is no reason for such a curve to be linear. That is, a more generally applicable formula is needed. Given the concave character seen in *Figure 11*, a simple and for most purposes significant representation can be provided by the quadratic equation:

$$\ln(\eta_{\text{blend}}/\eta_{\text{matrix}}) = a_0 + a_1 \ln(\eta_{\text{matrix}}/\eta_{\text{PLC}}) + a_2 \ln^2(\eta_{\text{matrix}}/\eta_{\text{PLC}}) \quad (4)$$

where a_0 , a_1 and a_2 are parameters for a given class of blends; the type of EP and the shear rate are implicit variables which define $\eta_{\text{matrix}}/\eta_{\text{PLC}}$. When such a master curve exists, the viscosity of an EP + PLC blend can be calculated from the viscosities of the pure EP matrix and the pure PLC. The curve shown in *Figure 11* represents equation (4) with the parameters $a_0 = 0.0859$, $a_1 = -0.6820$ and $a_2 = 0.2450$.

The change in behaviour between 15 and 20% PLC (or between 10 and 15% PLC) can be explained in terms of $\theta_{\text{LC limit}}$, a parameter discussed above. The phase diagram for pure PET/*x*PHB copolymers as a function of *x* shows²⁰ that its value (which is temperature-dependent) lies somewhere between 20 and 30% PLC. Needless to say, the presence and kind of an EP affects the location of $\theta_{\text{LC limit}}$. The phase diagram of PC + PET/0.6PHB blends in ref. 1 shows that, at ~20% of the PLC, an LC-rich phase, namely smectic B, appears. This fact provides additional confirmation of the importance of phase diagrams in PLC systems, as argued elsewhere^{1,3,12}. More specifically, it explained why the reduced coordinate plot according to equation (4) for PC-containing blends coalesces with other curves at 20 wt% PLC but not at 15% PLC. Fesko and Tschoegl⁴⁴ noted that rheologically complex behaviour is expected in two-phase systems unless, in a certain region of temperature and time or frequency, the behaviour is dominated by one or the other phase. Here the situation is further complicated by the fact that single PLC copolymer already forms two or more phases—or, in other words, constituents of different phases (LC-rich islands, LC-poor matrix) are connected by primary chemical bonds. The existence of LC-rich islands (or fibrils) is also confirmed by the morphology results reported in the next section. However, below $\theta_{\text{LC limit}}$ the LC sequences in the PLC are so diluted by 'their own' flexible PLC sequences as well as by entire flexible EP chains that the second phase is not formed. The system behaviour is strongly dependent on the kind of EP present in high concentration and there is no master curve for different EP + PLC pairs, even though the PLC is the same in all systems. Above $\theta_{\text{LC limit}}$ apparently the phase separation that takes place results in a rheological simplification. Probably the islands become elongated by shear and the channelling effect (already discussed

above) occurs. Thus, the presence of an LC-rich phase at 20% PLC affects all blends in a similar way. We recall Rule 5 of formation of hierarchical structures⁴⁰: assembling entities in a specified way one can achieve properties which a system of unassembled entities does not have.

We are also now able to explain the confusing statements of BKP¹¹ on the subject of the applicability range of their formula, our equation (1). It is now evident that their equation—or our more general equation (4)—is applicable only at LC concentrations $\theta \geq \theta_{\text{LC limit}}$. This is why the applicability ranges of these equations change from one blend system to another. Unless θ is high enough for the islands to form, LC sequences within the matrix-dominated phase have only limited capabilities to enforce their orientation tendencies on the entire blend system; we are back to the hypothesis of Fesko and Tschoegl⁴⁴. When a certain extent of orientation is imposed, systems containing various EPs begin to behave similarly. Then, if only differences in the viscosities of the pure EPs (η_{matrix}) are appropriately taken into account, a common or master curve results.

MORPHOLOGY

Given the manifestations of multiphase behaviour in rheological properties reported above, we have also studied the blend morphology by using a Nikon Optiphot optical microscope with a polarizing unit. The samples, with a thickness of several mm, were cut parallel to the flow direction on sections of injection-moulded plates using a Leica microtome. For each sample observations were made near the surface and also in the middle part of the plate. A selection of the micrographs so obtained is presented in *Figure 12*.

For all blends significant but similar effects of the presence of the PLC are evident. Since the microscopic observations pertain to sections of injection-moulded plates, a spatial structure gradient is easily observed. Specifically, in all cases the cold wall of the mould caused the skin effect, followed by a typical layer structure created by the flow forces and a more uniform structure in the middle of the flow, apparently with spherulites and fine LC-rich islands. Since we know that island formation requires $\theta_{\text{LC limit}}$ to be exceeded, a concentration gradient might be involved as well. As discussed above, the structurization created by the flow is important for the viscosity lowering by the PLC. In *Figure 1* in the companion paper¹ we have seen the morphology of the 80 wt% PC + 20% PLC blend. Apparently a typical amorphous state of pure PC was transformed into a skin-layer fibrillar gradient structure. We have already commented above on the secondary but still pertinent role of the LC sequences in the LC-poor matrix in viscosity lowering.

We recall here that pure PP already exhibits skin-core morphology, studied (for instance) diffractometrically for isotactic PP by Wenig and Herzog⁴⁵. For blends of the PLC with PVDF, PBT and PP, where all three EPs are semi-crystalline, we observe similar spatial structure gradients as for PC. Moving perpendicularly away from the wall, there is a gradual transition from the near-to-wall fibrils via elongated islands to approximately spherical islands. The diagonal of the bottom photo of *Figure 12b* is 200 μm , hence the diameter of the mixed islands in the centre of the flow varies from 1 to 20 μm .

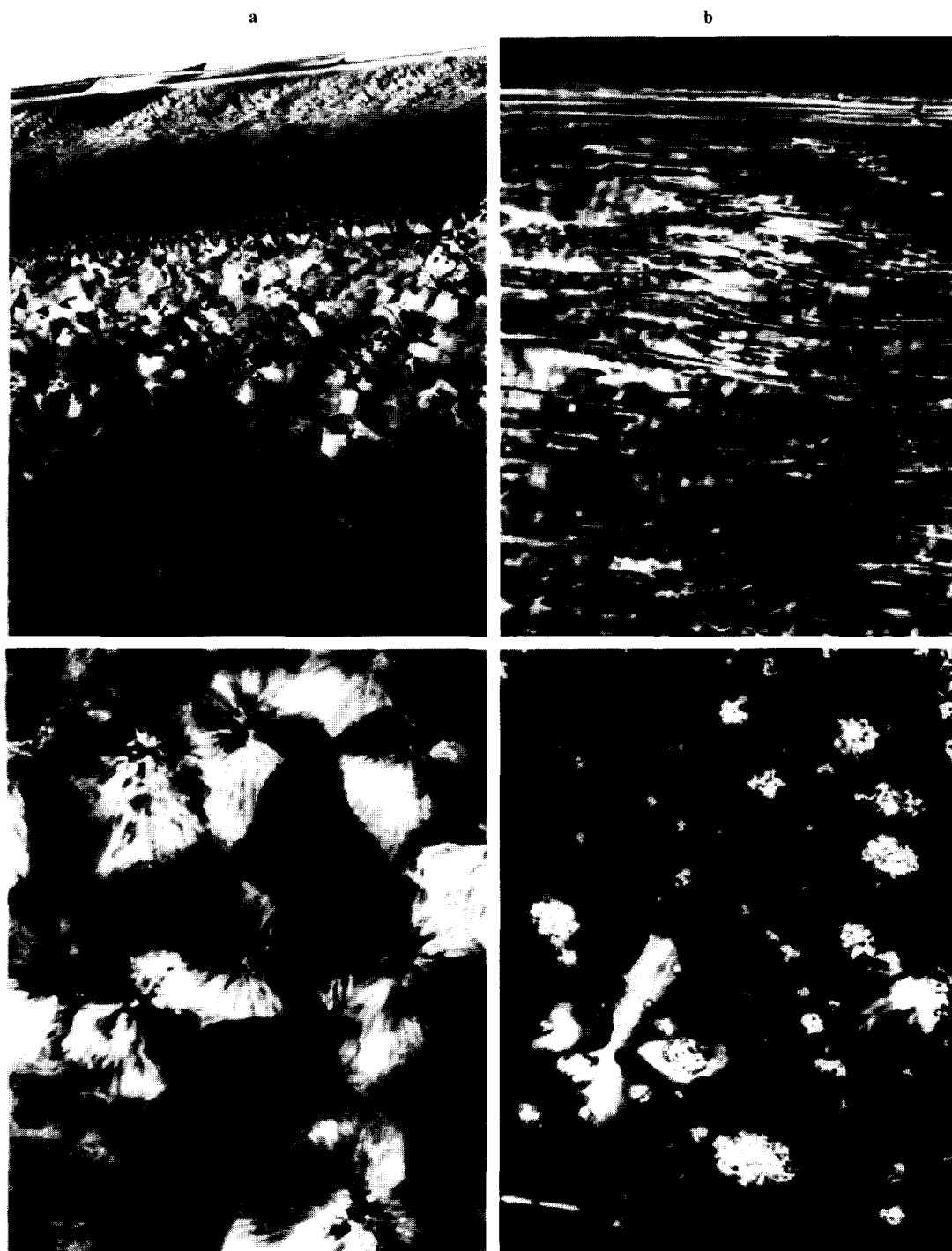


Figure 12 Morphology of the engineering polymers and EP + PLC blends on sections of injection-moulded plates with a thickness of 2 mm. All cuts parallel to the flow direction. (a) Pure PP: top, near the wall, the diagonal = $750\ \mu\text{m}$; bottom, middle, the diagonal = $200\ \mu\text{m}$. (b) PP + 15 wt% PLC: top, near the wall, the diagonal = $200\ \mu\text{m}$; bottom, middle, the diagonal = $200\ \mu\text{m}$

We recall further that the *pure* LC-rich islands have a diameter of approximately $1\ \mu\text{m}$ ^{15,40}. In these cases the middle (core) zone, with the primary well-developed structure in pure EPs (spherulites in PP visible in *Figure 12a*, bottom), change by the PLC addition into at least partly mixed EP spherulite LC-rich islands. We see in *Figure 12b* bottom white PP spherulites, rather small and irregular. The spherulites are limited in their growth by the LC-rich islands. It should be recalled that PP crystallizes extensively around 130°C , when PET/0.6PHB is already a solid; see *Table 1* and for more detail the phase diagram in the preceding paper¹.

Apparently the solid island surfaces serve as nucleating centres for the PP crystallization. This results in directional growth of the PP lamellae, approximately perpendicular to the island surfaces.

The situation is similar for PVDF and PBT. PVDF has the maximum of crystallization around 140°C , so that our PLC is a solid in this case as well. We do not include the other micrographs for brevity, and because of their similarity to those included, but the micrographs for PVDF show small and irregular PVDF spherulites. D.s.c. determinations show that the crystallization temperature of PVDF increases along with the PLC

concentration increase, confirming that the latter acts as a nucleating agent for the former, causing an increase in the number of spherulites along with a decrease in their sizes.

The very existence of the structure gradient still requires an explanation. The layer structure resulting from the shear flow in the zone near to the wall of the mould apparently persists. By contrast, the islands and possibly fine spherulite EP droplets dispersed in the core must have been created by elongation in the middle of the flow followed by a relaxation of the elongated flow zone. Overall, the morphology results reinforce the conclusion reached from the rheology of the melts.

CONCLUDING REMARKS

It is the anisotropic structure that permits lower viscosity in the LC-containing phases than in the isotropic polymer melts. We have found that addition of our PLCs to a series of EPs results in all cases in large decreases of the viscosity. In certain instances the viscosity of the blends was two to three times lower than that of the respective thermoplastic matrix. Thus, modification by our PLC results in a considerable increase of the processability of the EPs studied. Significant effects appear at PLC concentrations as low as 5 wt%.

The reason for the viscosity lowering is not the incompatibility of the blend components but the natural proclivity of pure PLC copolymers for orientation and for the formation of at least two phases. Since some compatibility or even miscibility is present in the solid state, we have a combination of good melt processability with the improvement of mechanical properties of EPs by blending with a PLC.

Engbert and Gedde⁴⁶ reported attempts to heal knit lines in injection-moulded PLCs; their main objective was randomization, i.e. counteracting the natural island formation and orientation processes. Island formation was an important factor in the development of a theory of hierarchical structures in materials such as PLCs⁴⁰. We now observe deformation of the islands by flow and also formation of layer/fibril structures near the die or the wall of the injection mould. As a consequence, the resulting materials have to exhibit strong anisotropy of mechanical and other properties. The anisotropy was found by mechanical drawing of a pure PET/0.3PHB copolymer²⁰; drawing up to 300% resulted in fourfold increases in the elastic tensile modulus and tensile strength. The anisotropy in the blends is similar, although lower because of the presence of the flexible EP chains.

Our study is limited to blends of a longitudinal PLC with EPs. It is known that different classes of PLCs exhibit different properties, since molecular structures are reflected in the macroscopic behaviour²⁻⁴. Studies of rheology of some combs such as that by KKS^{9,10} have been reported. Rheological studies of molten phases of PLCs belonging to other classes appear worthwhile.

A given PLC copolymer—or a blend containing such a copolymer—might or might not form two or more phases, depending primarily on the overall LC concentration. We have demonstrated that the applicability of the original BKP equations $\theta \geq \theta_{LC \text{ limit}}$. This constitutes one more conformation of the importance of $\theta_{LC \text{ limit}}$ as discussed in refs 1, 12 and 26, but now in rheology.

We have noted already that explanation of the rheological results for the PC + PLC blends would have been impossible without us having determined the phase diagram first¹.

ACKNOWLEDGEMENTS

Partial financial support for this work was provided by the Robert A. Welch Foundation, Houston, TX (grant no. B-1203). Discussions with Professor Lew Fایتelson and Dr Ernest Jakobson of the Institute of Polymer Mechanics of the Latvian Academy of Sciences in Riga, and with Professor Jukka J. Seppälä and Dr Markku T. Heino of the Helsinki Institute of Technology, are appreciated. Thanks are due to Dr Nandika Anne D'Souza of the University of North Texas for her insightful comments on the manuscript and also to a referee for helpful advice.

REFERENCES

- 1 Brostow, W., Hess, M., López, B. L. and Sterzynski, T. *Polymer* 1996, **37**, 1551
- 2 Brostow, W. *Kunststoffe* 1988, **78**, 411
- 3 Brostow, W. *Polymer* 1990, **31**, 979
- 4 Brostow, W. in 'Liquid Crystalline Polymers: From Structures to Applications' (Ed. A. A. Collyer), Elsevier Applied Science, London, New York, 1992, Ch. 1
- 5 Onsager, H. L. *Ann. NY Acad. Sci.* 1949, **51**, 627
- 6 DeLong, M. L. and Russo, P. S. *Macromolecules* 1991, **24**, 6139
- 7 de Abajo, J., de la Campa, J. G., Izu, P., Santamaria, A. and Tormes, M. *Polymer* 1995, **36**, 1683
- 8 Stenhouse, P. J., Vallés, E. M., Kantor, S. W. and MacKnight, W. J. *Macromolecules* 1989, **22**, 1467
- 9 Kannan, R. M., Kornfield, J. A., Schwenk, N. and Boeffel, A. *Macromolecules* 1993, **26**, 2050
- 10 Kannan, R. M., Kornfield, J. A., Schwenk, N. and Boeffel, A. *Adv. Mater.* 1994, **6**, 214
- 11 Borisenkova, E. K., Kulichikhin, V. G. and Platé, N. A. *Rheol. Acta* 1991, **30**, 581
- 12 Brostow, W., Hess, M. and López, B. L. *Macromolecules* 1994, **27**, 2262
- 13 Wissburn, K. F. *Faraday Disc.* 1985, **79**, 161
- 14 Wissburn, K. F., Kiss, G. and Cogswell, F. N. *Chem. Eng. Commun.* 1987, **53**, 149
- 15 Brostow, W., Dziemianowicz, T. S., Romanski, J. and Werber, W. *Polym. Eng. Sci.* 1988, **28**, 785
- 16 Menczel, J. and Wunderlich, B. *J. Poly. Sci.-Phys.* 1980, **18**, 1433
- 17 Menczel, J. and Wunderlich, B. *Polymer* 1981, **22**, 778
- 18 Crevecoeur, G. and Groeninckx, G. *Bull. Soc. Chim. Belg.* 1990, **99**, 1031
- 19 Crevecoeur, G. and Groeninckx, G. *Mater. Res. Soc. Symp.* 1990, **171**, 165
- 20 Jonah, D. A., Brostow, W. and Hess, M. *Macromolecules* 1993, **26**, 76
- 21 Flory, P. J. *Proc. Royal Soc. A* 1956, **234**, 60, 73
- 22 Abe, A. and Flory, P. J. *Macromolecules* 1978, **11**, 1122
- 23 Flory, P. J. and Ronca, G. *Mol. Cryst. Liq. Cryst.* 1979, **54**, 289, 311
- 24 Matheson Jr, R. R. and Flory, P. J. *Macromolecules* 1981, **14**, 954
- 25 Matheson Jr, R. R. *Macromolecules* 1986, **19**, 1286
- 26 Blonski, S., Brostow, W., Jonah, D. A. and Hess, M. *Macromolecules* 1993, **26**, 84
- 27 Brostow, W. and Walasek, J. *Macromolecules* 1994, **27**, 2923
- 28 Heino, M. T., Hietaoja, P., Vainio, T. and Seppälä, J. *J. Appl. Polym. Sci.* 1994, **51**, 259
- 29 Sukhaida, A., Doane, D. and Baird, D. G. *Polym. Eng. Sci.* 1990, **30**, 519
- 30 Shin, B. Y. and Chung, I. J. *Polym. Eng. Sci.* 1990, **30**, 22
- 31 La Mantia, F. P., Valenza, A., Paci, M., Magagnini, P. L., Podretti, U. and Rogero, A. *Polym. Eng. Sci.* 1993, **33**, 944

- 32 Geiger, K. 'Polymer Processing Society Sixth Annual Meeting', Nice, 1990, p. 10-09
- 33 Kulichikhin, V. G., Drevel, V. E., Kotova, E. A., Antipov, E. M., Godovsky, Yu. K. and Zuev, V. V. *Polym. Eng. Sci.* 1933, **33**, 889
- 34 Kenig, S. 'Polymer Processing Society Sixth Annual Meeting', Nice, 1990, p. 10-KN2
- 35 Ziabicki, A. 'Polymer Processing Society Sixth Annual Meeting', Nice, 1990, p. 05-KN1
- 36 Acierno, D., Amendola, E., Carfagna, C., Nicolais, L. and Nobile, R. *Mol. Cryst. Liq. Cryst.* 1987, **153**, 533
- 37 Kyu, T. and Zhuang, P. *Poly. Commun.* 1988, **29**, 99
- 38 Aiji, A. and Gignac, P. A. *Polym. Eng. Sci.* 1992, **32**, 903
- 39 Brostow, W., Kaushik, B. K., Mall, S. B. and Talwar, I. M. *Polymer* 1992, **33**, 4687
- 40 Brostow, W. and Hess, M. *Mater. Res. Soc. Symp.* 1992, **255**, 57
- 41 Brostow, W. and Samatowicz, D. *Polym. Eng. Sci.* 1993, **33**, 581
- 42 International Union of Pure and Applied Physics, *Physica A* 1978, **93**, 1
- 43 International Union of Pure and Applied Chemistry, 'Quantities, Units and Symbols in Physical Chemistry' (Ed. I. Mills), Blackwell Scientific Publications, Oxford, 1988
- 44 Fesko, D. G. and Tschoegl, N. W. *J. Polym. Sci. C* 1971, **35**, 51
- 45 Wenig, W. and Herzog, F. *J. Appl. Polym. Sci.* 1993, **50**, 2163
- 46 Engbert, K. and Gedde, U. W. *Progr. Colloid Polym. Sci.* 1992, **87**, 57