Reaction kinetics and chemo-rheology of poly(*p*-phenylenebenzobisthiazole) polymerization in the ordered phase

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The phenomenon of mesophase-enhanced polymerization of the rodlike polymer poly(*p*-phenylenebenzobisthiazole) at 15% by weight in polyphosphoric acid has been investigated. The reacting mixture becomes anisotropic at an early stage of the polymerization. The reaction rate increases significantly at the isotropic–nematic phase transition as the rods are aligned in positions more favourable for the condensation reaction to occur. The chemo-rheological properties at high shear rates ($\geqslant 10\,s^{-1}$), but not at low shear rates ($\leqslant 5\,s^{-1}$), also indicate the occurrence of the phase change. A systematic study of the effects of shear rate and temperature suggests that initial mixing of the monomer mixture below the polymerization temperature greatly influences the final achievable molecular weight of the polycondensation reaction.

(Keywords: poly(*p*-phenylenebenzobisthiazole); rodlike polymer; mesophase-enhanced polymerization; reaction kinetics; ordered phase; chemo-rheology)

INTRODUCTION

Polybenzazoles (PBZ), a class of aromatic, heterocyclic rigid rod polymers, have received increasing interest as advanced materials for applications requiring high thermal, oxidative and structural stability. Because of the rigidity of the backbone, these polymers can form ordered phases in solutions at high chain concentrations. Such orderability has been known to provide great advantages to the polymer processibility and the physical properties of the fabricated products. Exceptional mechanical properties can be obtained in fibres and films fabricated from these lyotropic polymers. A tensile strength of 4.2 GPa (607 000 psi) and a tensile modulus of 330 GPa (48 million psi) have been reported for heat-treated fibres spun from poly(*p*-phenylenebenzobisthiazole) (PBT)[1], one of the most rigid polymers in the PBZ family.

Benefits can also be realized when polymer synthesis is performed in the ordered phase. Initial research on the synthesis of PBT was conducted in polyphosphoric acid (PPA) at concentrations below 3 wt% of polymers to avoid the extremely high shear viscosity of the reacting media. Such polymerization mixtures remained isotropic throughout the polymerization, but the maximum attainable molecular weight was low, and the polymer had to be isolated and redissolved at higher concentration for fibre processing. The practical need for higher efficiency motivated attempts to polymerize at higher concentrations. At greater than 5 wt%, liquid crystalline domains were formed during the polymerization of PBT, and the reacting mixture remained tractable. The reaction kinetics and final attainable molecular weight were greatly enhanced. Moreover, the processibility of the dope was improved significantly.

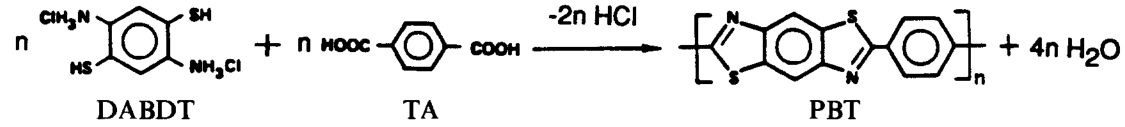
A study on the polymerization kinetics of another rodlike polybenzazole, poly(*p*-phenylenebenzobisoxazole) (PBO), at concentrations below the liqiud crystalline phase transition indicates that the rate of increase in molecular weight with reaction time decreases with the molecular weight of the rodlike chains[2]. This result suggests that the polymerization rate is diffusion limited because the rotational diffusivity depends strongly on the molecular length. In the ordered phase, however, the molecules are already aligned in positions favourable for condensation, and the polymerization rate is therefore expected to increase. We call this phenomenon mesophase-enhanced polymerization (MEP).

Because of the scientific as well as technological importance of polycondensation of rodlike polymers in the ordered phase, we investigated MEP in more detail. We describe a quantitative study on the reaction kinetics and chemo-rheological properties of PBT polycondensation at high concentration under conditions that cause liquid crystalline phase transition to occur during the polymerization. The effects of phase change, shear and temperature are discussed.

EXPERIMENTAL

Material preparation

The synthesis of PBT, reported in detail previously[3], is typically performed by the condensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and terephthalic acid (TA) in PPA following the removal of hydrogen chloride:



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Preparation of DABDT monomers follows the rigorous purifying procedures described in the literature[3]. In all experiments, the monomer concentration is chosen to yield a final polymer concentration of 15% by weight. In this reaction, PPA serves as a solvent, catalyst and dehydrating agent. Hydrogen chloride is first completely removed from the reaction mixture of DABDT in PPA before the addition of 10 μm TA particles. Solid P_2O_5 is then added according to the P_2O_5 adjustment method[4] to ensure adequate reaction conditions for a high degree of polymerization. Benzoic acid of 0.50 mol% based on DABDT is used as endcapping agent to control the final molecular weight of the polymer. After the original mixture of DABDT and PPA at 90°C is stirred for sufficient time to remove the hydrogen chloride, the mixture of monomers, benzoic acid, PPA and P_2O_5 is ready for polymerization at temperatures above 150°C.

Polymerization kinetics

Most of the polymerization runs in this study follow a temperature profile known to produce satisfactory conditions for the polymerization. The monomer mixture is first heated from 90 to 180°C at a rate of 0.75°C min^{-1}. When the mixture reaches 180°C, the temperature is maintained at 180°C throughout the polymerization. In a few cases, different temperature profiles are used to investigate their effects on the reaction.

All monomer mixtures are prepared in 500 ml glass reactors with three attached ground glass joints. This reactor design allows constant mechanical stirring of the reaction mixture and continuous argon purge. During polymerization, small aliquots of the reaction mixture are removed periodically from the glass reactor. The reactor also allows removal of samples for analysis without exposing the reacting mixture to air or introducing other contaminants. A heated oil bath is used to control the reactor temperature.

A portion of the removed aliquot is placed on a microscope slide for direct observation under an optical microscope. The remaining portion is precipitated in deionized water, and the residual PPA is thoroughly removed by extraction with water in a Soxhlet apparatus. The polymer is completely dried under reduced pressure at >130°C overnight.

The weight-average molecular weight, M_w, of PBT can be determined by measuring the intrinsic viscosity of the polymer in dilute concentrations and using the following Mark–Houwink relationship[5]:

$$[\eta] = 4.86 \times 10^{20} (d_H^{0.2}/M_L)(M_\eta/M_L)^{1.8} \quad (1)$$

$$M_\eta = M_w(M_z/M_w)^{4/9} \quad (2)$$

The intrinsic viscosity $[\eta]$ is in dl g^{-1}; d_H is the hydrodynamic diameter of a chain element taken to be 7×10^{-7} cm for PBT; M_L is the mass per unit length, which is 2.15×10^9 cm^{-1}; M_z is the z-average molecular weight, and M_z/M_w is 1.3 for PBT.

Experimentally, the intrinsic viscosity of PBT solutions is measured at 30.0°C using an automated Cannon–Ubbelohde microdilution viscometer. The solutions are prepared by dissolving dried PBT in freshly distilled methane sulphonic acid (MSA), and the intrinsic viscosity is measured within 48 h after the solutions are prepared. Four successive dilutions are used to extrapolate the measurements of specific and inherent viscosities to infinite dilution. The solution efflux times are chosen to fall within 1.1 to 1.5 times the solvent efflux time. No kinetic correction is necessary because the efflux times are longer than 100 s.

Rheology

Rheological measurements on the polymerizing mixtures are performed using a Rheometrics RMS-605 mechanical spectrometer. Because of the high sensitivity of the reaction mixtures to oxygen and moisture, a modified cone-and-plate fixture is used to prevent exposure of the reacting mixture to moisture over a long period (at least several hours). The fixture, made of Hastelloy C to resist acid corrosion at elevated temperature, consists of additional outer, concentric rings on both the cone and the plate such that dried, high-temperature-grade silicone oil can be introduced to form a barrier to moisture and oxygen as shown in *Figure 1*. The diameter of the plate is 25 cm and the cone angle is 0.1 radian.

About 1 ml of the prepared monomer mixture at 90°C is removed from the bulk sample under nitrogen purge and loaded onto the cone-and-plate fixture carefully to minimize contaminant introduction. The flow cell is preheated to 90°C to avoid reprecipitation of the dissolved components. The sample is kept under a nitrogen blanket until the flow cell is closed and sealed with silicone oil. The temperature of the sample is then increased according to a predetermined temperature profile to initiate the polymerization. Different temperature profiles have been followed to investigate the effect of temperature on the polymerization.

The effect of shear is studied by subjecting the polymerizing media to continuous steady shear throughout the reaction (including the initial temperature ramp) at shear rates from 0.01 to 50 s^{-1}. The rheometer is programmed to record the torque reading and calculate the shear viscosity at about two-minute intervals. At the end of each run, the dope is removed from the flow cell for molecular weight determination using intrinsic viscosity measurements.

After a series of polymerization runs, the remaining bulk monomer mixture is polymerized in the glass reactor using a similar temperature profile for comparison purposes.

RESULTS AND DISCUSSION

Polymerization kinetics

Figure 2 shows the change in the intrinsic viscosity as a function of reaction time of 15 wt% PBT in PPA. The broken line shows the temperature profile throughout the reaction starting from 150°C. The intrinsic viscosity can

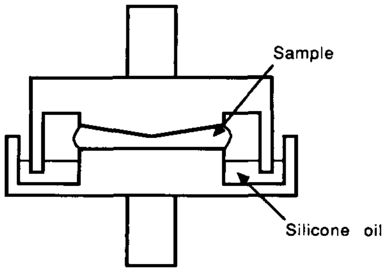


Figure 1 Modified cone-and-plate with moisture seal

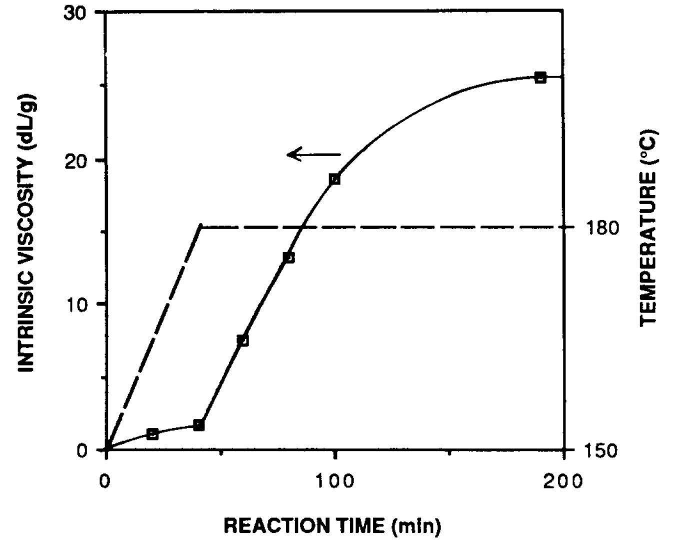


Figure 2 Increase in polymer intrinsic viscosity during polycondensation of 15 wt% PBT in PPA

be converted to the weight-average molecular weight (M_w) using equation (1). The number-average degree of polymerization (x_n) can then be determined by the molecular weight of the repeat unit (M_0) and M_w:

$$x_n = 2(M_w/1.3M_0) \qquad (3)$$

The factor of 2 is needed because two condensing species form each repeat unit. The constant 1.3 within the parentheses is used to convert weight-average to number-average molecular weight by assuming a polydispersity of 1.3 (refs. 2 and 6). *Figure 3* plots x_n as a function of reaction time.

The salient feature of *Figures 2* and *3* is the sharp increase in the intrinsic viscosity and x_n at about 40 min (t_1) after time $t=0$ at 150°C. The slope of the curve immediately following t_1 is increased significantly. *Figure 4* shows the rate of polymerization, $d(x_n)/dt$, which is calculated from the slope of the curve in *Figure 3* at the midpoint between data points. More than a five-fold increase in the polymerization rate is observed at the transition. In contrast, polycondensation of PBO at low concentrations (below 2 wt%) exhibits only a decreasing rate of polymerization with increasing molecular weight throughout the entire reaction[2].

Direct observation indicates that, at the same time that the kinetic rate increases abruptly, the reacting dope becomes stir-opalescent, indicating the onset of a liquid crystalline phase in the dope. Analysis of thin samples under a polarized optical microscope shows that the dope is birefringent at $t \geqslant t_1$ but isotropic at $t < t_1$. The abrupt increase in the reaction rate is therefore interpreted as a quantitative description of the mesophase-enhanced polymerization by which the enhancement in kinetics is due to the alignment of rigid rods in the ordered phase.

It is coincidental that t_1 appears very close to the point at which the temperature reaches 180°C. We suspect that the abrupt increase in the kinetic rate is a result of the temperature profile and not due to the phase transition. However, previous study on polycondensation of PBO in the isotropic phase does not indicate any discontinuous change in the polymerization rate with temperature from 150 to 185°C[2]. Therefore, the observed change in the kinetics is too dramatic to be due to the gradual increase in temperature as performed in our experiments.

The polymer molecular weight at which the phase transition occurs can be compared with theoretical predictions using Flory's statistical mechanical model for athermal systems[7]. The model predicts that ϕ_c, the critical volume fraction of rodlike solute at which phase separation first occurs, is related to the axial ratio (x) of monodisperse rods by:

$$\phi_c = (8/x)(1-2/x) \qquad (4)$$

In our polymerization of PBT, the specific gravity of PBT is about 1.5 and that of PPA is 2.0. ϕ_c is therefore 0.19 and x is 40 according to equation (4). Experimentally, we observed a phase change when the number-average molecular weight of PBT is less than 6016 dalton. If we assume 0.7 nm to be the molecular diameter of PBT, and 1.25 nm to be the length of a repeat phenylenebenzobis-

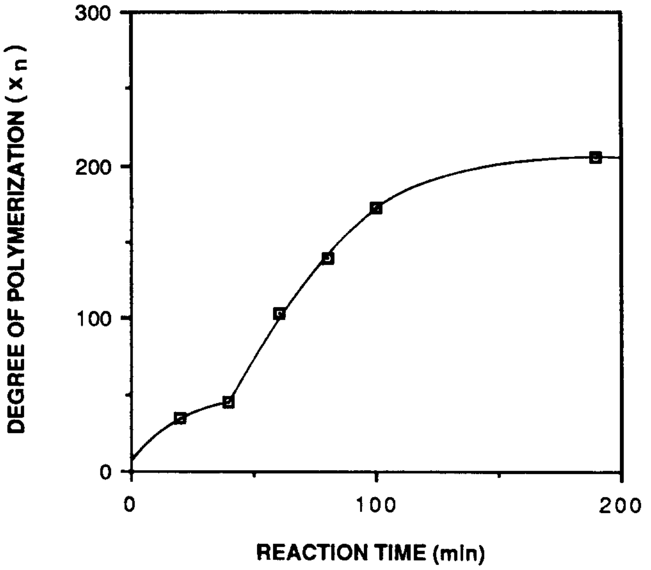


Figure 3 Degree of polymerization as a function of reaction time for polycondensation of 15 wt% PBT in PPA

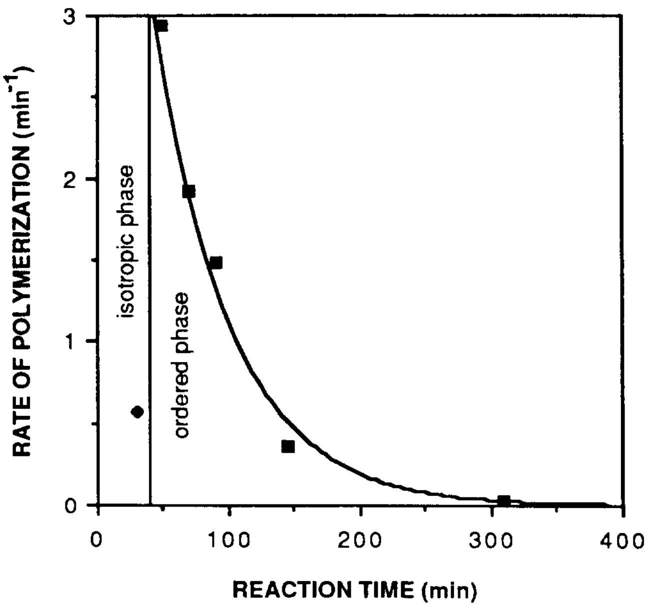


Figure 4 Rate of polymerization as a function of reaction time for polycondensation of 15 wt% of PBT in PPA

thiazole unit based on crystallographic results on model compounds[8], the critical number-average axial ratio of PBT is calculated to be about 40 ($x_n = 45$) when the phase transition was first detected. Our experimental result compares favourably with the theoretical value.

Flory's theory also predicts a wholly anisotropic phase to occur when $x \sim 12.5/\phi$ for a monodisperse system. Calculations based on this model indicate a narrow biphasic region, when a complete nematic phase at $x = 66$ ($x_n = 73$) for PBT. Although a broader biphasic region is expected for polydisperse systems[9], the rapid polymerization rate at 180°C makes it difficult to determine accurately the breadth of the biphasic region.

Figure 4 suggests that, in the liquid crystalline phase, the polymerization rate versus reaction time can be empirically described by an exponentially decaying function, and the degree of correlation of such curve fitting is 0.99. The decrease in the rate of polymerization is a function of the amount and reactivity of endcapping agent, the reactivities of side reactions, and possibly the molecular weight of the polymers. More research is needed to understand better the physical significance of such exponential dependence.

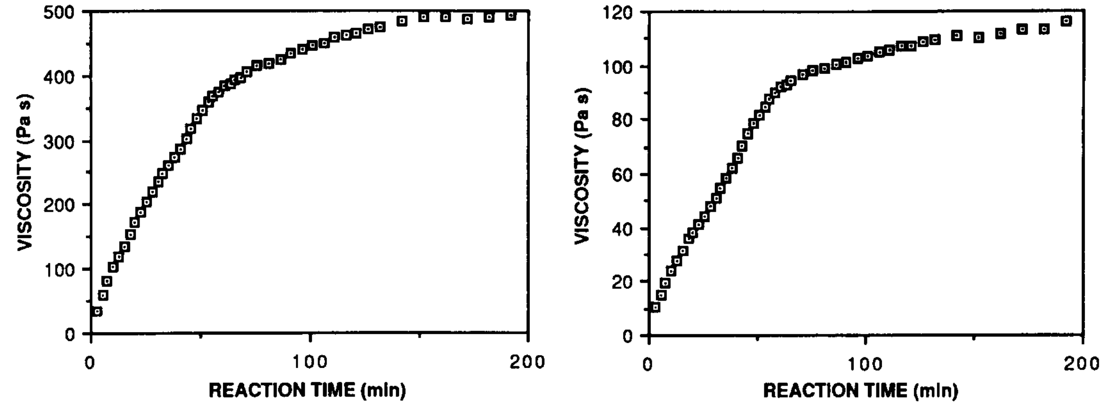
Chemo-rheological properties

The rheological behaviour of lyotropic, rigid rod macromolecules near the isotropic–nematic phase transition has been a subject for numerous theoretical as well as experimental investigations[10]. In most experimental studies, the shear viscosity is measured as a function of concentration at a fixed molecular weight and temperature. Characteristically, the viscosity first increases with concentration, reaches a maximum near the phase transition, then decreases in the nematic phase region at high concentrations.

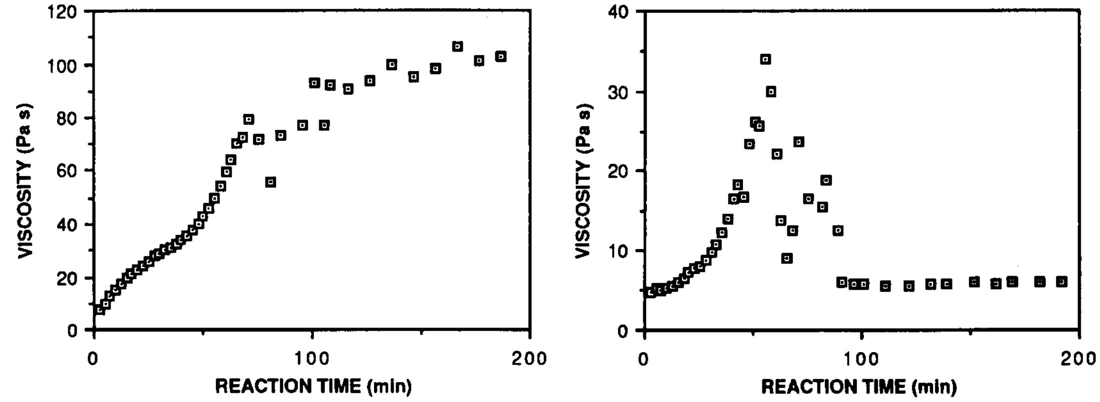
In the PBT polymerization, the volume fraction of rods stays constant while the molecular weight and the temperature vary with time. The shear viscosity of the reacting media, monitored by the rheometer in cone-and-plate geometry, is shown in *Figure 5* for shear rates of 1, 5, 10 and 50 s^{-1}. The temperature profile in these experiments follows that in the kinetic study described in the last section: an increase of 0.75°C min^{-1} from 90 to 180°C, followed by a hold at 180°C throughout the remaining time of the reaction.

In all the experiments shown in *Figure 5*, the specified shear was applied starting from 90°C. Previous experience indicates that no appreciable reaction can be detected until the temperature reaches at least 150°C; data acquisition therefore begins at 150°C. At shear rates of 1 s^{-1} and higher, the resulting dopes at the end of all runs appear green and stir-opalescent, and it is easy to draw long fibres from the dope. These are indications of moderately high molecular weight polymers in the ordered phase.

To our surprise, the rheological data at low shear rates (1 and 5 s^{-1}) provide little indication of the isotropic–nematic phase transition. The viscosity increases monotonically and quite smoothly with reaction time. At higher shear rates (10 and 50 s^{-1}), a slight break in slope in the viscosity function near 40 to 50 min is observed. This break is very close to, and therefore suspected to be related to, the phase transition observed in the kinetic study.



(a) Shear rate = 1.0 s^{-1} (b) Shear rate = 5 s^{-1}



(c) Shear rate = 10 s^{-1} (d) Shear rate = 50 s^{-1}

Figure 5 Shear viscosity versus reaction time during polymerization of 15 wt% PBT in PPA at shear rates of 1.0, 5.0, 10 and 50 s^{-1}

In *Figures 5a* and *5b*, the viscosity increases very slowly or levels off at long reaction time. *Figures 5c* and *5d*, however, exhibit more unusual features beyond the phase transition. *Figure 5c* shows a dip in viscosity at 81 min. *Figure 5d* shows a dip at 66 min, followed by a dramatic drop in viscosity after 90 min. The origins of these sudden reductions in viscosity are unclear. Some may be due to changes in the degree of order in the nematic phase, and some may be artefacts resulting from secondary flows, sample slippage or sample being spun out of the flow cell due to the high rotational rate of the cell. Without further experimental evidence, we believe that the decrease is unlikely to be a manifestation of the biphasic–nematic phase transition.

Polymerizations performed at shear rates below 1.0 s^{-1} were less successful than those at higher shear rates. At 0.1 s^{-1}, the final greenish dope shows poor fibre-forming properties. Below 0.1 s^{-1}, the final material appears brownish-orange with black streaks, and no fibre can be drawn. Such appearance suggests low molecular weight materials. *Figure 6* illustrates the intrinsic viscosity of the final dope versus the shear rate at which the polymer is polymerized. This figure suggests that the shear rate has significant effects on the final molecular weight.

We also observe that the degree of polymerization of PBT polymerized in the cone-and-plate cell is significantly less than those polymerized in the glass reactor. The same batch of monomer mixture polymerized in the glass reactor after the series of shear experiments were conducted yields an intrinsic viscosity of 16.7 dl g^{-1}; no higher than 13 dl g^{-1} is obtained in the rheometer as shown in *Figure 6*. This discrepancy may be due to one or more of the following: (1) contaminants (e.g. oxygen, moisture) introduced during loading of the monomer mixture onto the rheometer; (2) contaminants on the surface of the flow cell; (3) surface effects of the flow cell; and (4) differences in monomer mixing in early stages of the polymerization. However, this problem does not invalidate our earlier observation that the phase change effect does not seem to manifest itself in the low shear viscosity function since the final dopes from the rheometer are indeed liquid crystalline.

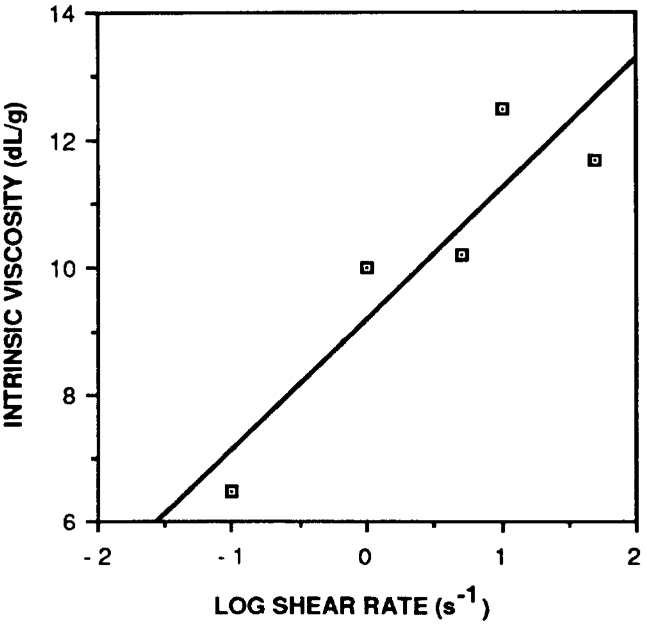


Figure 6 Semilogarithmic plot of the final polymer intrinsic viscosity versus the combination of shear rate used for the polymerization

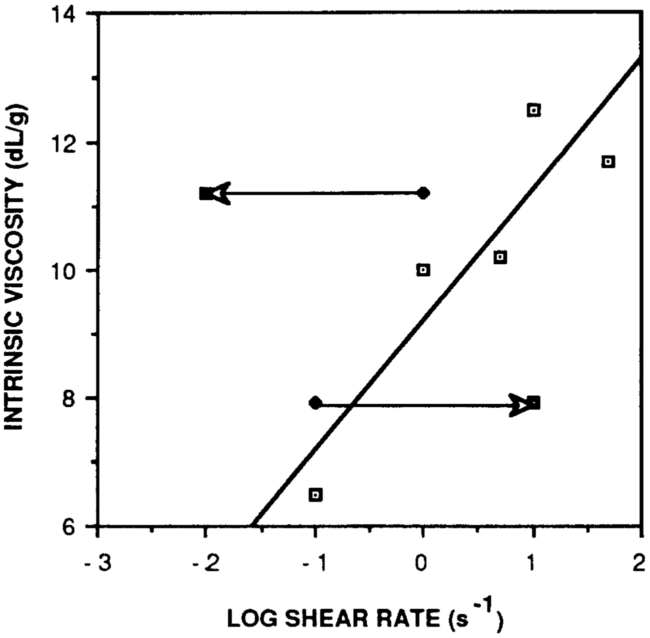


Figure 7 Semilogarithmic plot of the final polymer intrinsic viscosity versus the shear rates used for the polymerization. The arrows indicate direction of shear rate change at 150°C

The shear dependence on the final degree of polymerization could be a result of an enhancement in molecular alignment during shearing, or simply better mixing of the monomer mixture or the reacting medium. To distinguish between these two possible mechanisms, we performed two experiments in which a combination of shear rates was used. In one polymerization run, the monomer mixture was first sheared at 1 s^{-1} from 90 to 150°C, and the shear rate was reduced to 0.01 s^{-1} starting at 150°C throughout the polymerization. This shear profile yielded polymer with a final intrinsic viscosity of 11.2 dl g^{-1}, although the shear rate of 0.01 s^{-1} alone has been found to be inadequate to achieve successful polymerization. In a second polymerization run, a shear rate of 0.1 s^{-1} was applied below 150°C and 10 s^{-1} above 150°C, and the resulting polymer exhibited an intrinsic viscosity of only 7.9 dl g^{-1}. These results suggest that a mixing effect, not molecular alignment, is the underlying reason for the shear dependence of the degree of polymerization.

Figure 7 illustrates the results on final intrinsic viscosity versus shear rates used for polymerizing the monomers. The arrows indicate the direction of change in shear rate at 150°C. Good correlation with previous polymerization results can be obtained when the initial shear rates, not the final ones, are used in a plot of the intrinsic viscosity versus shear rate.

We investigated the effects of different temperature profiles on the polymerization at a constant shear rate of 1 s^{-1}. *Figure 8* shows three profiles. In the first one, described previously, the final PBT shows an intrinsic viscosity of 10.0 dl g^{-1}. The second profile shows a sharp increase from 90 to 180°C in 20 min, and we only found a brownish-black residue, which appears to be a degradation product of the monomer at the end of the polymerization. The third profile contains an increase from 90 to 150°C in 20 min, a hold at 150°C for 100 min, and a sharp increase from 150 to 180°C. This profile

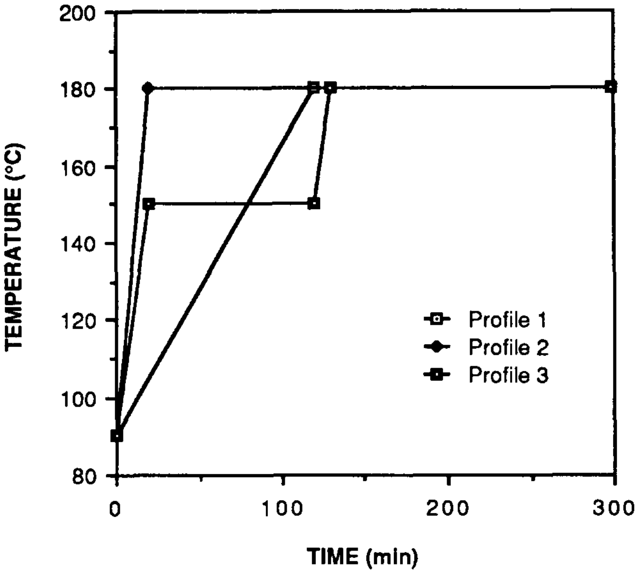


Figure 8 Three temperature profiles used for polymerizing 15 wt% PBT in PPA

produced the best results, a final polymer intrinsic viscosity of 12.6 dl g^{-1}, which is one of the highest obtained among all polymerization runs performed in the rheometer.

These data indicate that the temperature profile during the mixing period below 150°C has a drastic influence on the polymerization, whereas the temperature profile above 150°C has less effect on the resulting product. The results of the temperature and shear rate studies can be explained by a rapid polymerization for which an intimate mixture is critical and by the decreased sensitivity of oligomeric species to thermal decomposition.

CONCLUSIONS

This study demonstrates quantitatively the enhancement in the polymerization kinetics of PBT when ordered domains form in the polymerizing solution. Chemorheological measurements at low shear rates throughout the polymerization, however, are a poor indication of the dramatic change in the reaction rate due to the phase change. At higher shear rates, the viscosity function exhibits features believed to result from the phase transition. Moreover, at long time and high shear, the viscosity displays characteristics that have uncertain origins. These results are difficult to simulate by model study because the shear viscosity is a complicated function of the temperature, molecular weight, P_2O_5 content, shear rate and the degree of order in the nematic phase. Currently, there is no satisfactory unified theory on the rheology of rodlike polymers that can account for these complicated effects.

The shear rate and temperature effects on the polymerization products were not anticipated. Our data indicate that these parameters are most influential in the premixing stage (below 150°C) and much less influential in the polymerizing stage (above 150°C). Such results suggest that, once the monomer mixture is well dispersed initially, the polymerization can be performed to satisfaction under a wide range of reaction conditions. Conversely, if good mixing is not achieved in the early stage when the viscosity is low, later mixing is much less effective after PBT starts to polymerize significantly. We suspect that the dissolution of TA particles may be the limiting step to good mixing in the early stage.

Several unanswered questions have risen in this study. We have not yet been able to resolve the discrepancy in the final degree of polymerization between the glass reactor and rheometer runs. We are now investigating the possible effects of contamination and flow cell geometry.

ACKNOWLEDGEMENTS

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