Dissolution behaviour of thermotropic liquid-crystalline polyesters in 3,5-bis(trifluoromethyl)phenol and pentafluorophenol

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(Received 28 April 1992; revised 13 July 1992)

Determining η_{sp}/c as a function of time has been used to investigate rates of dissolution and stabilities of solutions of liquid-crystalline polyesters (LCPs). The dissolution behaviour of commercial LCPs and prepolymers, post-condensates and pelletized LCPs prepared in-house has been studied in 3,5-bis(trifluoromethyl)phenol (BTFMP) and pentafluorophenol (PFPh). All of the investigated polyesters dissolved in both solvents. Optimum temperatures for dissolution appeared to be 25°C for BTFMP and 40°C for PFPh. Dissolution times ranged from 10 to 40 h. The solutions remained stable for at least 80 h. Dissolution of post-condensates is very difficult. Fortunately, by reducing the crystallinity, they dissolved more readily in both solvents without modifications of the molecular structure. Therefore, determining reliable molecular parameters of LCPs seems to be possible in these solvents.

(Keywords: liquid-crystalline polymers; thermotropic polyesters; molecular characterization; dissolution behaviour; solvents)

INTRODUCTION

Thermotropic liquid-crystalline polyesters (LCPs) have received a lot of attention in recent years as a new class of high-performance materials. As a result of this, several types of aromatic copolyesters have been commercialized by different companies (among others, Vectra® by Hoechst-Celanese, Xydar® by Amoco, and Ekonol® by Sumitomo), while several other companies are still involved in R&D programmes on LCPs.

The reason behind this interest is the unique property profile (like tensile strength, flexural modulus, heat distortion and continuous use temperature) that can be obtained with these materials. In addition to these properties, the excellent flow properties of these LCPs, which result in short processing times, can be mentioned. Furthermore, these LCPs have good barrier properties, good dimensional stability and excellent chemical resistance to a variety of organic solvents, acids and bases.

However, the latter fact is a major drawback with respect to the production and characterization of these materials, since they are insoluble in nearly all organic solvents. This seriously handicaps the determination of molecular parameters (such as molecular weight), which are required both for quality control purposes (in production) and for the understanding of the relations between process conditions and material properties.

So far, the literature on the solubility properties of LCPs has been limited. Hoechst-Celanese claims the use of pentafluorophenol (PFPh) as a solvent for their material, this solvent being used at elevated temperatures (60–80°C)[1]. Lenz advises, among others, the use of PFPh as a solvent for LCPs[2].

Although this solvent seems to work well for Vectra, it does not seem to be as good for the higher-melting Xydar and Ekonol. For example, Kinugawa and Kise[3] described the use of PFPh for an LCP with the composition *p*-hydroxybenzoic acid/*p*,*p'*-biphenol/terephthalic acid/isophthalic acid (molar ratio 16:4:3:1), which reportedly dissolves only in an autoclave at 200°C. Bayer claims the use of fluoromethylphenols as solvents for liquid-crystalline polyesters, in particular 3,5-bis(trifluoromethyl)phenol[4]. However, there is no additional information given on the possibilities and limitations of these solvents. Moreover, no insight into the time required to dissolve the polymer and into the stability of the prepared solutions has been obtained.

Because of the impact of molecular parameters on properties, there is a strong need for reliable methods to characterize LCPs. In this study, we aimed at an understanding of the dissolution behaviour of some commercial materials (Vectra, Xydar and Ekonol) as well as the crucial causes behind the (apparent) insolubility of some LCPs. Additionally, we studied the dissolution behaviour of LCPs prepared on in-house laboratory-scale equipment.

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0032-3861/93/030557-05

EXPERIMENTAL

Materials

The commercial thermotropic copolyesters Xydar SRT300 and SRT500 (copolymers of *p*-oxybenzoyl and oxybiphenyleneterephthaloyl units; from Amoco, USA), Ekonol E200 (copolymer composed of *p*-hydroxybenzoic acid, aromatic dicarboxylic benzoic acid and biphenol; from Sumitomo Chemical Co., Japan) and Vectra A900 (copolyester based on *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid; from Hoechst-Celanese, USA) were used as received.

Synthesis

The laboratory-scale LCP under investigation (STA) is based on 2 parts *p*-hydroxybenzoic acid (HBA; Bayer, Germany), 1 part *p,p'*-biphenol (BP; Bayer, Germany), 0.98 parts terephthalic acid (TPA; Amoco, USA) and 0.02 parts isophthalic acid (IPA; Amoco, USA).

The prepolymer (LMWSTA) was prepared by reaction of the *in situ* formed acetate esters of HBA and BP with dicarboxylic acid monomers by an acidolysis reaction. The acetic acid liberated during this reaction was readily removed. The copolyester, of intermediate molecular weight, was subsequently subjected to a final reaction in the solid state to increase the molecular weight (HMWSTA). Many aromatic (co)polyesters that show thermotropic behaviour have been prepared and reported, as described particularly in the patent literature[5,6].

Pelletized material (PELSTA) was prepared by extrusion of HMWSTA on a co-rotating twin-screw extruder (ZSK 30), using the following conditions: a temperature of 370–410°C, a screw speed of 60 r.p.m. and a throughput of $7\,kg\,h^{-1}$.

Viscometry

The solvent pentafluorophenol (PFPh, >99%; Janssen Chimica, Belgium) was used as received, while the other solvent 3,5-bis(trifluoromethyl)phenol (BTFMP, 97.7%; Yarsley Fluorchemicals Ltd, UK) was distilled prior to use. Intrinsic viscosity measurements were performed with an Ubbelohde capillary viscometer having an internal diameter of 0.5 mm and a length of 15 cm. The flow times were measured using a viscotimer (Lauda). Because flow times were relatively long ($t_0 > 100$ s in PFPh and 140 s in BTFMP), the correction for kinetic energy could be ignored. The samples were dissolved in the viscometer reservoir under various conditions, and the solutions were diluted by adding fresh solvent.

Quench procedure

A Hereaus tube oven was used for the quench procedure. The sample holder consisted of a massive cylindrical pipe in which a narrow hole was present for the sample. The sample holder fitted very well into the heated pipe of the oven. By means of this set-up, a quick and reliable heat transfer was ensured. A thermocouple was inserted into the sample holder.

First, the oven including the holder was set to the required temperature, i.e. 400°C. Subsequently, the sample holder was placed just outside the oven and the sample, wrapped in aluminium, was put into the holder. Finally, the sample holder was placed in the oven again. During this procedure, the temperature remained stable within 3°C. After this melting procedure the sample holder was taken from the oven and turned over to transfer the sample onto a cold metal plate. The final sample treatment could be carried out within 10 s.

RESULTS AND DISCUSSION

Dissolution behaviour of Xydar SRT300

It should be emphasized that a stable dilute solution of the LCP must be obtained in order to determine molecular parameters. Hence, an experimental method must be available to measure the stability of the obtained solutions. Measuring the flow time of a very dilute solution of a polymer in an Ubbelohde viscometer is an excellent method to gain insight into the time required for a polymer to dissolve and the stability of the solution obtained. By carrying out this type of measurement, a so-called dissolution/degradation curve can be obtained.

First, the flow time of the solvent (blank, t_0) is determined. Subsequently, the polymer sample is added to the solvent, which is stirred continuously, and finally η_{sp}/c is measured as a function of time. Generally the dissolution/degradation curve can be divided into four characteristic regions, as indicated in *Figure 1*. In region 1 an increasing value of η_{sp}/c as a function of time is observed, because the polymer dissolves. After reaching a maximum value, η_{sp}/c decreases (region 2) until a constant level is reached. This decrease might be caused by dissolution of entangled molecules. Region 3 is characterized by a constant value of η_{sp}/c. In region 4 a decrease of η_{sp}/c is observed. This decrease must be attributed to chain scission caused by oxidation or hydrolysis.

In *Figure 2*, the dissolution/degradation curves of Xydar SRT300 in BTFMP (25°C) and PFPh (40°C) are represented. From these results, it appears that the polymer dissolves slowly in either solvent. The dissolution times are 20 h in PFPh and 40 h in BTFMP. Region 2 cannot be recognized, indicating that disentanglement is not the rate-determining step in the dissolution process. The solutions remain stable for at least 80 h. So, after 80 h region 4 has not been reached.

In order to optimize the dissolution conditions, η_{sp}/c was determined at elevated temperatures. These conditions were also recommended by Bayer[4]. However, Kinugawa and Kise[3] reported that the solubility decreased with increasing temperature. The results are presented in *Figure 3*. These results indicate that the solvent quality decreases significantly with increasing temperature for Xydar SRT300 in either solvent and in

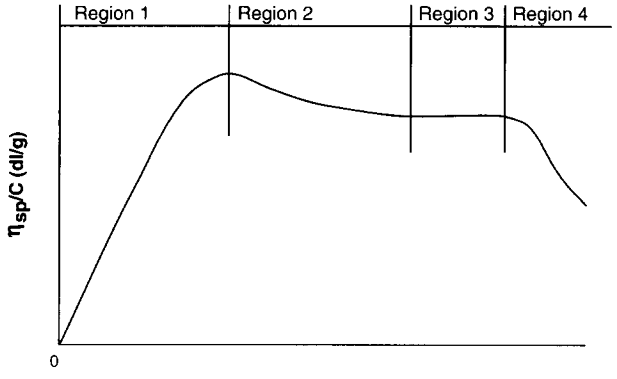

Figure 1 Schematic representation of a dissolution/degradation curve

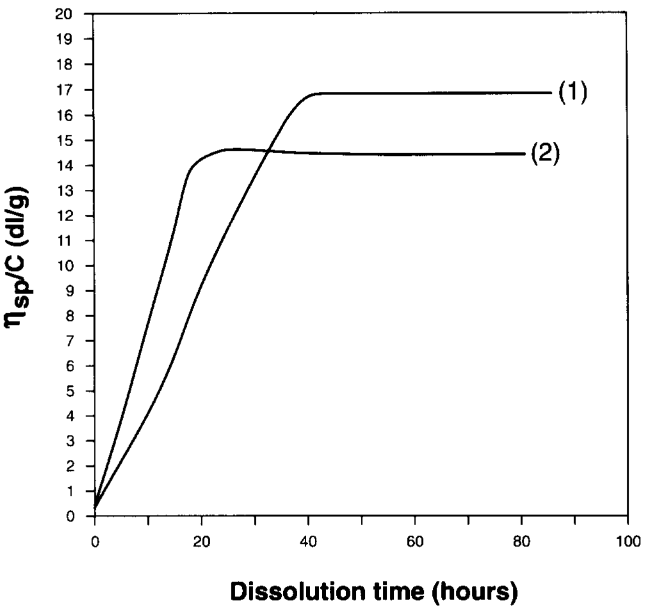

Figure 2 Dissolution/degradation curves of Xydar SRT300 in (1) BTFMP (25°C, $c=0.0239\,\mathrm{g\,dl^{-1}}$) and (2) PFPh (40°C, $c=0.0257\,\mathrm{g\,dl^{-1}}$)

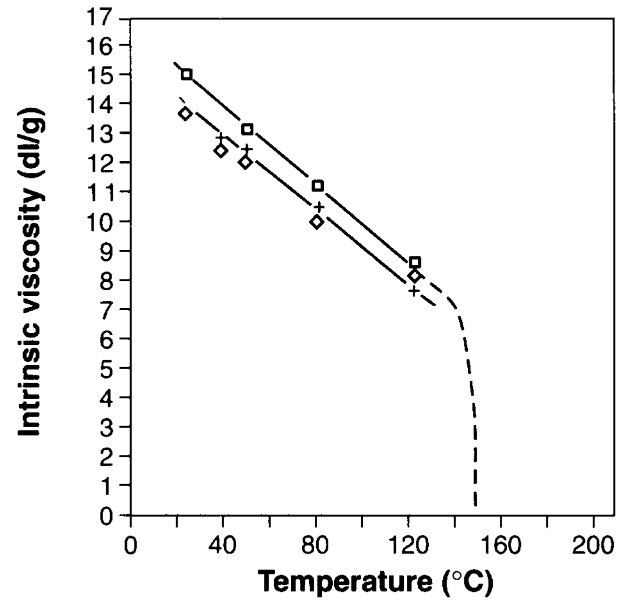

Figure 3 Temperature dependence of the intrinsic viscosity of Xydar SRT300 in (□) BTFMP, (+) PFPh and (◇) a mixture of BTFMP and PFPh (1:1, w/w)

a mixture of solvents (1:1). From a separate experiment it even appeared that Xydar SRT300 is insoluble at 140°C in both BTFMP and PFPh.

From these results, the most favourable temperature at which to dissolve Xydar SRT300 appears to be 25°C in BTFMP and 40°C in PFPh. The temperature for PFPh is somewhat higher than for BTFMP since the melting temperature for PFPh is 34°C. Under these conditions η_{sp}/c is 16.8 $\mathrm{dl\,g^{-1}}$ for Xydar SRT300 in BTFMP and 14.5 $\mathrm{dl\,g^{-1}}$ in PFPh, indicating a slight difference in solvent quality, although it should be realized that there is a temperature difference and hence a solvent quality difference.

These results unambiguously indicate that the fully aromatic polyester, having a very high melting temperature (430°C), dissolves in both BTFMP and PFPh at ambient temperature. The rates of dissolution are relatively slow compared to the rates obtained for flexible polymers. The solutions obtained are stable for at least 80 h.

Dissolution behaviour of STA

Prepolymer (LMWSTA). The dissolution conditions applied for Xydar SRT300 were also used for the dissolution of LMWSTA. In *Figure 4*, the dissolution/degradation curve of LMWSTA in BTFMP (25°C) is represented. From these results, it appears that even after 140 h no real steady state has been reached, although the gradual increase of η_{sp}/c as a function of time seems to be of minor influence on the final level. The increase is 0.06 in 80 h. The solutions seem to remain stable. Unfortunately, the prepolymer did not dissolve completely in either BTFMP or PFPh. One component also present in the prepolymer, i.e. terephthalic acid, did not dissolve in either solvent. So, the incomplete dissolution of the prepolymer might be attributed to an increased content of terephthalic acid in the insoluble part. However, from infra-red (i.r.) and high-performance liquid chromatographic (h.p.l.c.) analysis of the hydrolysed product, no significant differences according to composition of the soluble and insoluble parts could be determined. The soluble part was worked up by precipitation and filtration. Subsequently, a dissolution/degradation curve was determined. This result is also presented in *Figure 4*. From the results it is inferred that this part of the prepolymer dissolves very easily within 12 h. The solution remains stable for at least 70 h. Obviously, the insoluble material of the prepolymer contains structures that prevent the theoretically soluble chains from dissolving. Perhaps the chains have to diffuse from a kind of network or highly crystalline regions and dissolve very slowly. Until now the cause of this phenomenon has remained unexplained, and no further attempts were made to investigate this anomalous behaviour since the insoluble part was only 2%. Therefore, this was of minor influence on the determination of η_{sp}/c.

Post-condensate (HMWSTA). The final polymer (HMWSTA) was obtained by solid-state post-condensation of the prepolymer (LMWSTA). During this reaction

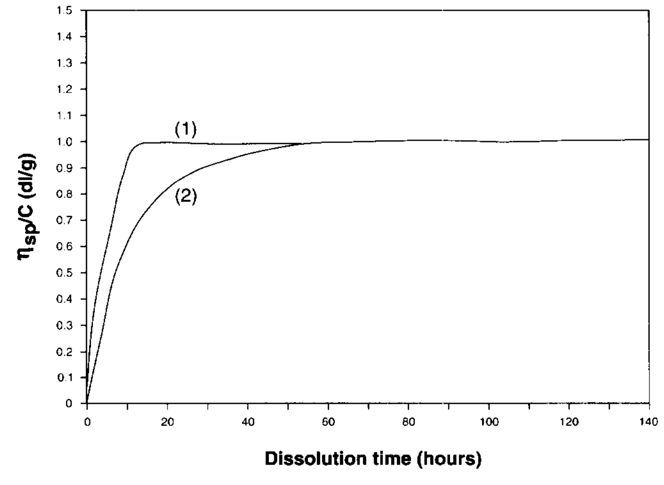

Figure 4 Dissolution/degradation curves of (1) prepolymer soluble part ($c=0.413\,\mathrm{g\,dl^{-1}}$) and (2) prepolymer (LMWSTA; $c=0.388\,\mathrm{g\,dl^{-1}}$) in BTFMP (25°C)

the temperature of the reactor increased gradually. It is believed that, owing to this temperature gradient, the polymer particles obtain a morphology gradient that might prohibit dissolution. This expectation was verified since the polymer appeared to be completely insoluble in either solvent. Some possibilities were considered to explain this behaviour: (1) skin–core effects; (2) degree of crystallinity and/or type of crystal structure (hexagonal *versus* orthorhombic).

The first possibility is not likely as a general cause for this phenomenon, since thorough crushing of the material did not result in a significantly better dissolution behaviour. The second possibility seemed to prevent the polymer from dissolving. *Figure 5* shows the d.s.c. curves of the original HMWSTA and the quenched (1 min, 450°C) HMWSTA. From these results, it is inferred that the crystallinity changes drastically. In *Figure 6*, the dissolution/degradation curves of both products are given. In contrast to the original sample, the quenched sample dissolves relatively easily.

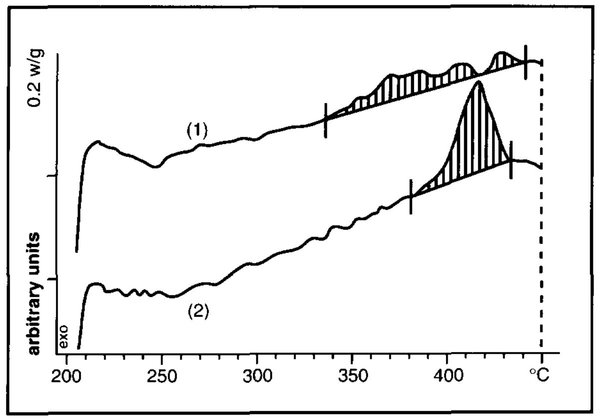

Figure 5 Heating curves (d.s.c.) of (1) quenched post-condensate (soluble) and (2) post-condensate (insoluble)

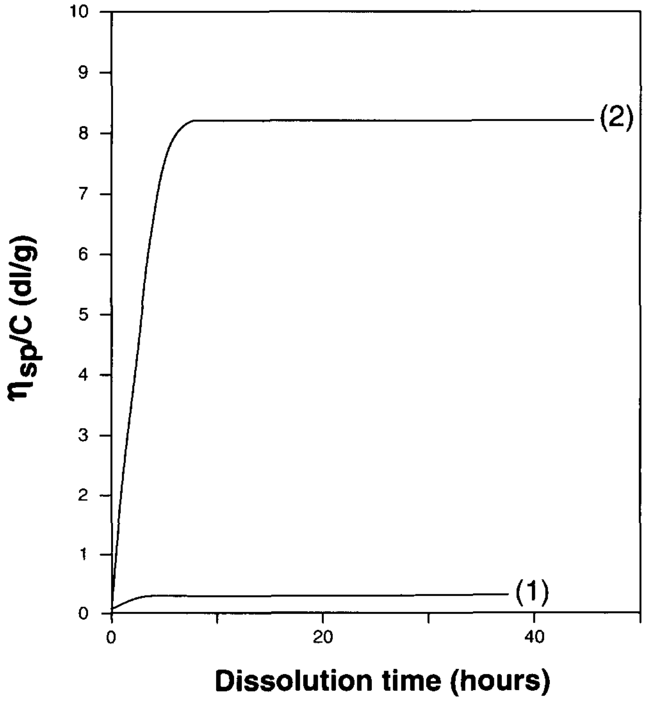

Figure 6 Dissolution/degradation curves of (1) post-condensate (HMWSTA; $c = 0.0239\,\mathrm{g\,dl^{-1}}$) and (2) quenched post-condensate ($c = 0.0209\,\mathrm{g\,dl^{-1}}$) in PFPh (40°C)

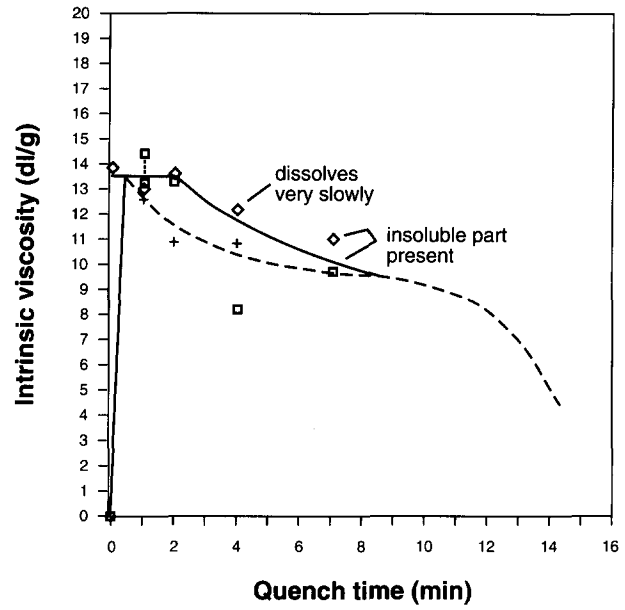

Figure 7 Intrinsic viscosities (after 144 h dissolution of the polymer) of (◇) Xydar SRT300 at 450°C, (□) HMWSTA at 450°C and (+) HMWSTA at 460°C, as a function of quench time

However, during the quench procedure both condensation and degradation reactions might occur, resulting in, respectively, too high and too low viscosities. In order to determine the influence of these processes, HMWSTA and Xydar SRT300 were quenched using various temperatures and times. The products obtained were characterized by single-point measurements. The intrinsic viscosity was calculated using the Huggins linear equation with $k_H = 0.3$. The results are given in *Figure 7*. From these results, it appears that degradation occurs at 460°C. At 450°C no decrease of the intrinsic viscosity is observed provided the quench times are less than 3 min. Hence, no significant influence of condensation or degradation reactions can be detected. However, if longer quench times are applied, the intrinsic viscosity decreases dramatically, and in some cases even insoluble material can be observed in the solution.

From these experiments, it appears unequivocally that it is possible to dissolve LCPs having very high melting points, provided that the proper quench conditions are applied to change the crystallinity.

Pellets (*PELSTA*). In order to pelletize the material, HMWSTA powder was melted during extrusion and finally cooled down relatively fast. This cooling procedure is also a kind of quenching. As a consequence, these kinds of materials will dissolve relatively easily in both solvents. The final levels of η_{sp}/c are approximately equal to the level of the post-condensate (HMWSTA), indicating that no degradation or condensation has occurred during the pelletization process.

Dissolution behaviour of various other LCPs

The product Ekonol E2000 did not dissolve in BTFMP at 25°C. Probably, the final polymerization step was a post-condensation. Quenching this material, using similar conditions as applied for the Xydar SRT300, resulted in a material that dissolved readily.

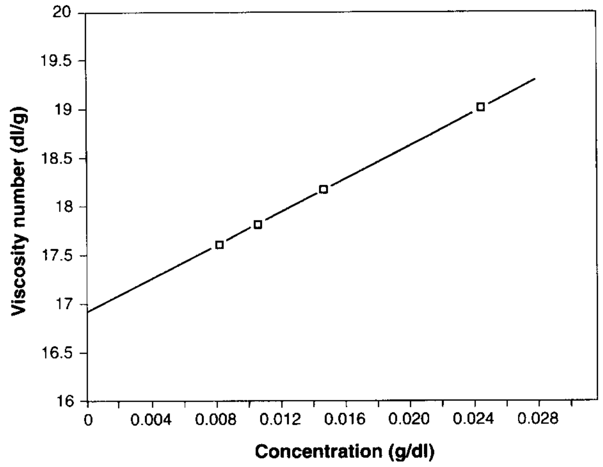

Figure 8 Huggins plot of Xydar SRT300 in BTFMP (25°C)

The Xydar SRT500 (a grade slightly modified compared with the Xdar SRT300 to lower the melting point and improve the processing behaviour) dissolved readily without any additional treatment in BTFMP ($\eta_{sp}/c = 13.5\,\mathrm{dl\,g^{-1}}$ with $c = 0.0329\,\mathrm{g\,dl^{-1}}$).

One exception during our investigation was the dissolution behaviour of Vectra A900. This material dissolved without any problem in BTFMP at 25°C, showing $\eta_{sp}/c = 7\,\mathrm{dl\,g^{-1}}$ with $c = 0.0245$ g/100ml. However, the polymer did not dissolve at 40°C in PFPh. Fortunately, at 80°C, the temperature recommended by Hoechst-Celanese[1], the polymer dissolved in PFPh. The strong temperature dependence of the intrinsic viscosity remained. Cooling down the solution to 40°C did not result in precipitation. The polymer remained in solution.

Choice of solvent

To combine the advantages of the separate solvents, mixtures of BTFMP and PFPh were prepared. Unfortunately, these mixtures showed no additional advantage over BTFMP at 25°C or PFPh at 40°C. The time needed to dissolve Xydar SRT300 was 50h and for PELSTA 45h. HMWSTA did not dissolve completely and LMWSTA dissolved very slowly. This dissolution behaviour is very similar to the behaviour in BTFMP. In the case of a mixture of the solvents, the intrinsic viscosity showed a strong temperature dependence, as represented in *Figure 3*. These results reconfirm that BTFMP is the preferred solvent for these kinds of LCPs.

Concentration dependence of η_{sp}/c

In order to obtain a molecularly dispersed solution, the concentration of the polymer must be as low as possible. As a rule of thumb, the product of the concentration and the intrinsic viscosity should be less than unity. Assuming that this rule for flexible chains is also valid for stiff chains, the concentration must be less than $0.05\,\mathrm{g\,dl^{-1}}$ if $[\eta] \approx 20\,\mathrm{dl\,g^{-1}}$. In *Figure 8*, the Huggins plot is presented for Xydar SRT300 in BTFMP. The initial concentration was $0.03\,\mathrm{g\,dl^{-1}}$. It appears that the concentration dependence of η_{sp}/c is linear. The value of the Huggins constant is approximately 0.3.

CONCLUSIONS

BTFMP is recommended as the best solvent for LCPs for the following reasons:

(1) From a thermodynamic point of view, BTFMP is a slightly better solvent than PFPh, since at the same temperature the values of the intrinsic viscosities are slightly higher in BTFMP than in PFPh.

(2) The handling of PFPh is more difficult, since the melting point of PFPh is 34–36°C.

(3) All tested materials dissolve in BTFMP at 25°C, while there is an exception (Vectra) for PFPh at 40°C.

The crystalline structure of the materials seems to be the crucial factor determining the dissolution behaviour. The molar mass and skin–core morphology played a relatively unimportant role. LCPs that seemed to be insoluble dissolved readily after quenching, i.e. after reduction of the crystallinity. Provided the proper quench conditions were applied, no alterations in molecular structure were observed and the intrinsic viscosity of even Xydar-type materials could be determined.

If the equipment for size exclusion chromatography (s.e.c.) can withstand the corrosive properties of BTFMP, it should also be possible to determine the molar-mass distributions of LCPs. In this case, special attention must be paid to the calibrations. This forms the scope of future investigations.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge permission by DSM Research to publish this work.

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