



The Effect of Benzyl Alcohol on the Glass-Transition Temperature and Dyeing Behaviour of Wet Courtelle S by Means of DMA

D. Aitken, S. M. Burkinshaw & D. M. Price*

Department of Colour Chemistry and Dyeing,
The University, Leeds LS2 9JT, UK

(Received 14 May 1991; accepted 18 June 1991)

ABSTRACT

Dynamic mechanical analysis has been used to demonstrate the plasticizing action of benzyl alcohol on wet Courtelle S tow. The extent of plasticization, as measured by reduction in T_g of the wet fibre, was found to correspond to the amount of benzyl alcohol adsorbed by the fibre; the maximum extent of plasticization coincided with the maximum concentration of benzyl alcohol adsorbed by the fibre, which, in turn corresponded to the aqueous solubility of the carrier under the application conditions employed. The extent of the enhancement of uptake of CI Basic Blue 3 onto acrylic fibre was found to be proportional to the extent of plasticization, a maximum value being reached at the aqueous solubility of the carrier.

1 INTRODUCTION

At temperatures below the glass-transition temperature (T_g), amorphous or semi-crystalline polymers behave as rigid solids or glasses in which the segmental mobility of the polymer chains is minimal. As the temperature is increased, the segmental motion of the macromolecular chains increases, and, at high temperatures (above T_g), the material behaves as a highly rubbery liquid. The parameter T_g denotes the temperature at which the transition from glassy to rubbery behaviour occurs and is attended by marked changes in the mechanical, electrical, and thermodynamic

* Courtaulds Research, 101 Lockhurst Lane, Coventry CV6 5RS, UK.

properties of the polymer. Several techniques, namely, differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA), are commonly employed to determine the T_g of polymers, such methods recording the property–temperature response of the polymer from which the position of T_g can be identified by some convenient point on the resulting property–temperature plot.

The temperature T_g is of great importance with regard to the dyeing of acrylic fibres with basic dyes; dyeing must be carried out at temperatures above T_g since, owing to the virtual absence of segmental mobility at temperatures below T_g , little, if any dye diffusion occurs below the T_g of the fibre. Although the use of carriers is mostly confined to polyester and triacetate fibres, their effects on the dyeing of acrylic fibres have been discussed by several authors.^{1–13} Of the numerous suggestions that have been made over many years to explain carrier action, only one has been widely accepted, namely, that carriers plasticize or reduce the T_g of the fibre.

Although the effect of temperature on the physical properties of dry fibres has received much attention, relatively little work has been carried out under dyebath (i.e. wet) conditions owing to practical difficulties that attend its measurement. Many of the methods previously employed^{14–20} have been critically reviewed by Fuzek,²⁰ who concluded that monitoring the change in elastic modulus of a fibre with temperature gave the most reliable results.

The aim of this work was to use DMA to determine the effect of a model carrier, benzyl alcohol, on the T_g of acrylic fibre under aqueous conditions and to examine the relationship between this parameter and dyeability with a cationic dye.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Fibre

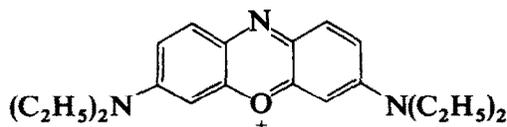
A commercial sample of Courtele S tow supplied by Courtaulds Fibres was used. The fibre was scoured prior to use by immersion in a stirred, aqueous (distilled-water) solution containing 0.5 g/litre Sandozin NIE (Sandoz) and 0.5 g/litre trisodium phosphate for 120 min at 40°C with a liquor-to-goods ratio of 40:1. The scoured fibre was then thoroughly rinsed by using distilled water until the wash-off was of constant pH (6.0) and allowed to dry in the open air.

2.1.2 Benzyl alcohol

Laboratory-grade benzyl alcohol was used throughout this investigation as a model carrier for acrylic fibre.

2.1.3 Dye

A sample of pure Maxilon Blue 5G (I) (Ciba-Geigy) (CI Basic Blue 3) was kindly supplied by Courtaulds Research, plc. The purity of the dye was checked by dissolving a known mass in boiling, anhydrous methanol and filtering, while hot, by means of a sohxlet extractor, to remove any inorganic impurities. The resulting solution was cooled and the methanol removed by rotary evaporation. The dye solid was then dissolved in a small quantity of



CI BASIC BLUE 3 (CI 51004)

distilled water by heating and the ensuing solution filtered, while hot, to remove any organic impurities; the filtrate was slowly cooled to induce crystallization. Since there was no appreciable difference between the extinction coefficients of aqueous solutions of the recrystallized dye and the starting dye, it was concluded that the original dye was pure.

All other reagents were of Analar-grade purity.

2.2 Equipment

The dynamic mechanical properties were measured at a constant frequency of 1 Hz and a constant oscillation amplitude of 0.3 mm (peak–peak) by using a Du Pont Instrument 983 Dynamic Mechanical Analyzer interfaced to a 9900 Series Computer Thermal Analyzer (Du Pont Instruments, USA). For the purposes of this work, a novel design of clamp assembly was employed²¹ whereby a bundle of filaments was tensioned between the jaws of a fixed holder while the driven arm of the DMA was used to bow the midpoint of the sample in a dual-cantilever action. Since the damping factor $\tan \delta (E''/E')$, is independent of both sample geometry and, to a first approximation, instrument calibration, the change in $\tan \delta$ as a function of temperature can be used to monitor the viscoelastic behaviour of the sample. In order to determine the T_g of wet fibres, a stainless-steel liner was fitted inside the DMA oven and, by turning the instrument on one side and filling this liner with water, the fibre sample could be completely immersed and heated at a controlled rate without the fibres drying out. A heating rate of 2°C per minute was found to be satisfactory even with the presence of water in the oven liner. Mechanical agitation of the water gave little improvement in heat transfer and was not employed owing to increased noise in the instrument output.

2.3 Procedures

2.3.1 Treatment of acrylic-fibre tow with benzyl alcohol

A 50-cm³ aliquot of a stock aqueous (distilled-water) buffer solution (270 cm³ 0.2M acetic acid/230 cm³ 0.2M sodium acetate) was placed in a 300-cm³ capacity stainless-steel dyepot. An appropriate volume of benzyl alcohol was then added to give a concentration of 10, 20, 30, 40, 50, 60, 70, or 80 g/litre and the solution made up to 100 cm³ by using distilled water; the pH of the treatment bath was 4.5. The sealed dyepot was housed in a Zeltex Polycolor PC1000 laboratory dyeing machine (Zeltex, Switzerland) and the treatment bath allowed to reach thermal equilibrium at 80°C. A sample (1 g) of scoured acrylic-fibre tow was then added and treatment continued for 30 min at this temperature. The dyepot was cooled to room temperature, and the fibre sample and the residual treatment liquor were removed and placed together in a sealed glass container to await analysis.

2.3.2 Determination of carrier uptake

Residual carrier was removed from a 1-g sample of tow, which had been treated with benzyl alcohol, by stirring in 50 cm³ of acetone at room temperature for 5 min, this being followed by rinsing in cold (distilled) water and drying in the open air. An accurately weighed portion (0.0200 g) was dissolved in 20 cm³ of DMF to which was added, after 20 min, 5 cm³ of glacial acetic acid. The solution was then centrifuged for 10 min at 2500 r/min by using a Gallenkamp Laboratory centrifuge (Gallenkamp, UK). A 5-cm³ aliquot was removed and a 1- μ l portion injected into a Varian 3300 Gas Chromatography (Varian, USA) interfaced to an NEC personal computer (NEC, Japan) by using a DB wax Megabore column (film thickness 1 μ m, length 30 m) with the column maintained at 150°C and the injector at 200°C. Nitrogen was used as carrier gas at a flow rate of 30 cm³/min and a flame-ionization detector, at 250°C, was employed. Each determination was limited to a duration of 5 min, with the benzyl alcohol having passed after 2.55 min. The system was calibrated by using a range of concentrations of benzyl alcohol in acidified (20% v/v acetic acid) DMF, the peak area for each benzyl alcohol concentration being recorded. The concentration of carrier in each treated fibre sample (C_f) was determined by computation of the area of the benzyl alcohol peak obtained for each sample relative to the calibration data.

2.3.3 The effect of benzyl alcohol on dye uptake

A 50-cm³ aliquot of the stock aqueous acetic acid/sodium acetate buffer solution described above was placed in a 300-cm³-capacity stainless-steel dyepot. A 20-cm³ aliquot of a stock aqueous (distilled-water) dye solution

(7×10^{-3} mol/litre) was then added and an appropriate volume of benzyl alcohol added to give a concentration of 10, 20, 30, 40, 50, 60, 70, or 80 g/litre. The volume of the ensuing dyebath was next made up to 100 cm^3 by using distilled water (the dyebath had a pH value of 4.5), the dyepot was housed in a Zeltex Polycolor PC1000 laboratory dyeing machine, and the dyebath was allowed to reach thermal equilibrium at 80°C . A sample (1 g) of dry, scoured Courtelle S tow was then added and dyeing carried out for 30 min at this temperature. The dyed sample was removed, rinsed with warm water, and stirred in 50 cm^3 of acetone for 5 min at 20°C , followed by rinsing in cold (distilled) water to remove surplus dye and carrier. An accurately weighed portion (0.0200 g) of the dyed material was dissolved in 20 cm^3 of DMF, to which was then added 5 cm^3 of glacial acetic acid to prevent dyestuff decomposition, and the ensuing solution was diluted by using acidified DMF (20% v/v acetic acid/DMF) to reduce the absorbance of the solution to an appropriate (20% v/v acetic acid/DMF) to reduce the absorbance of the solution to an appropriate value. The absorbance of the diluted solution was measured at 649 nm (the λ_{max} of the dye in this medium) by using a Pye–Unicam PU 8600 uv/visible spectrophotometer (Philips, UK), and, by reference to the appropriate extinction coefficient, the concentration of dye in the fibre (D_f) was obtained.

2.3.4 Determination of T_g

The length of the fibre sample used was determined by the design of the clamps, the resulting tension in the bundle of fibres being set arbitrarily by hand. The T_g of Courtelle S tow that has been pretreated with benzyl alcohol was determined by securing a bundle of pretreated filaments that had been stored in a sealed glass container, immersed in residual carrier-treatment liquor, between the clamps of the DMA. The mounted sample bundle was then immersed in 400 cm^3 of distilled water and the wet fibres were heated over the temperature range 20 – 90°C . The position of T_g was taken as the point of maximum damping on the plot of $\tan \delta$ versus temperature.

2.3.5 Determination of the aqueous solubility of benzyl alcohol

A 50-cm^3 aliquot of the stock aqueous buffer solution described above was placed in a 300-cm^3 -capacity stainless-steel dyepot, to which was added 10 cm^3 (10.42 g) of benzyl alcohol. The resulting dispersion was diluted to 100 cm^3 by using distilled water and the sealed dyepot then housed in a Zeltex Polycolor PC1000 laboratory-scale dyeing machine. The temperature of the agitated dyepot was raised to 80°C and this temperature maintained for 2 h, after which time, the contents of the dyepot were placed in a conical flask, which was suspended in a preheated water bath set at 80°C . The dispersion was allowed to settle for 60 min, and a 10-cm^3 aliquot was then

removed by using a preheated pipette and diluted to 100 cm^3 with distilled water. The absorbance of the resulting solution at 258 nm (the λ_{max} of benzyl alcohol in this medium) was measured by using a Pye–Uvicam PU 8600 uv/visible spectrophotometer, and, by reference to the appropriate extinction coefficient, the solubility of the carrier was determined.

3 RESULTS AND DISCUSSION

The T_g of Courtelle S tow in distilled water had previously been determined, by using the modified DMA technique described above,^{21,22} to be 72°C ; Fig. 1 clearly shows the marked plasticizing action of benzyl alcohol on wet Courtelle S tow as evidenced by the reduction in the T_g of the wet fibre. This finding concurs with those of other workers, who have demonstrated, by using various techniques, the plasticizing action of benzyl alcohol on polyacrylonitrile fibres.^{2,4,6,8-13,22} The non-linear relationship between T_g reduction and benzyl alcohol concentration (Fig. 1) shows the presence of a maximum value of 29°C and also indicates that this value corresponded to the aqueous solubility of the carrier at 80°C (0.568 mol/litre ; 61.4 g/litre), the temperature at which treatment with benzyl alcohol had been carried out. Figure 2 shows that uptake of benzyl alcohol by the fibre at 80°C increased with increasing concentration up to the aqueous solubility of the carrier, after which uptake decreased with further increase in concentration of benzyl alcohol. It can therefore be argued that the observed reduction in T_g that accompanied an increase in concentration of carrier applied to the fibre up to 0.555 mol/litre (60 g/litre) (Fig. 1) is due to a corresponding increase in

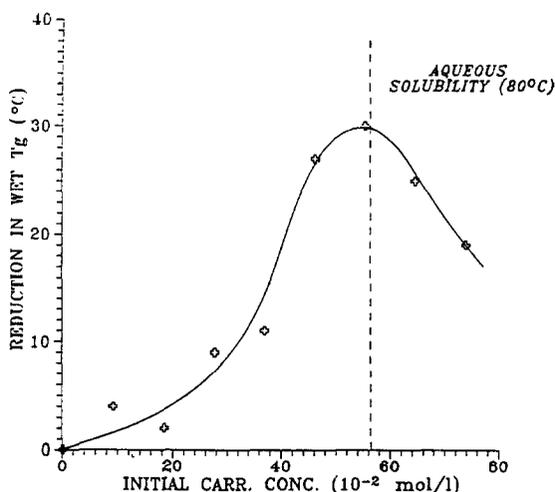


Fig. 1. The effect of benzyl alcohol on the T_g of wet Courtelle S.

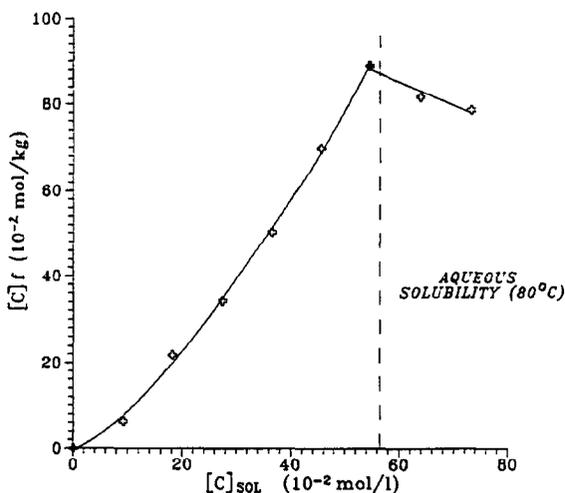


Fig. 2. The uptake of benzyl alcohol onto Courtelle S at 80°C.

concentration of benzyl alcohol adsorbed by the substrate. The maximum reduction in T_g that occurred at 60 g/litre benzyl alcohol corresponds to the maximum amount of carrier adsorbed by the fibre (Fig. 2), which, in turn, corresponds to the solubility of benzyl alcohol in water at 80°C. The observed increase in T_g that occurred at concentrations of carrier in excess of 60 g/litre (Fig. 1) is due to the aqueous solubility of benzyl alcohol having been surpassed, under which conditions, the carrier has greater affinity for the saturated, aqueous benzyl alcohol phase present in the treatment bath than for the fibre. Consequently, at benzyl alcohol concentrations in excess of 60 g/litre, carrier uptake by the substrate decreases with increasing concentration and thus T_g increases.

Essentially, a plasticizer functions as a diluent of polymeric substrates, its presence disturbing the packing of the polymer chains, as a result of which segmental mobility is increased by means of a reduction in inter-chain bonding. Thus, in order to operate, the plasticizer must be adsorbed by the polymer, and, in general, the extent of plastization will increase with increasing concentration of plasticizer in the substrate. Figure 3 clearly shows the plasticizing action of benzyl alcohol on the acrylic fibre; the extent of plasticization (i.e. T_g reduction) increases with increasing concentration of benzyl alcohol in the fibre (C_f), the maximum extent of plasticization corresponding to the maximum amount of the carrier adsorbed by the fibre (i.e. point F in Fig. 3, which corresponds to an applied carrier concentration of 60 g/litre). Points G and H in Fig. 3, which correspond to applied benzyl alcohol concentrations of 70 and 80 g/litre, respectively, show that, when employed at concentrations above its aqueous solubility at 80°C, the amount of benzyl alcohol adsorbed by the fibre decreases, resulting in a

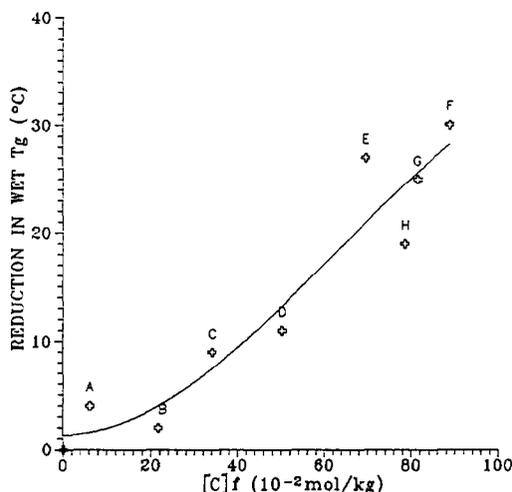


Fig. 3. Relationship between plasticization and benzyl alcohol uptake.

corresponding reduction in the extent of plasticization. The results shown in Fig. 1–3 therefore demonstrate that benzyl alcohol acts as a diluent of the acrylic fibre, the extent of plasticization (T_g reduction) increasing with increasing concentration of the carrier in the substrate.

The enhancement of uptake of CI Basic Blue 3 that occurred when dyeing had been carried out in the presence of benzyl alcohol (Fig. 4) can be attributed to the plasticizing action of the carrier on the fibre. The shape of the curve in Fig. 4 is virtually identical to that of Fig. 1 and shows that

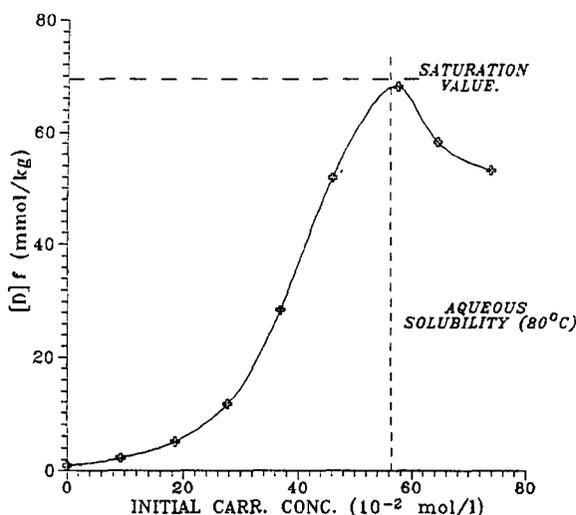


Fig. 4. Variation in dye uptake with initial benzyl alcohol concentration.

maximum dye uptake onto Courtelle S tow in the presence of benzyl alcohol corresponded to the maximum reduction in wet T_g obtained for the fibre in the presence of the carrier. Thus, the observed increase in uptake of CI Basic Blue 3 that occurred in the presence of up to 60 g/litre of benzyl alcohol can be attributed to an increase in plasticization of the wet fibre owing to an increase in concentration of the carrier adsorbed by the fibre. The maximum value of dye uptake that occurred at 60 g/litre of benzyl alcohol corresponds to the maximum amount of carrier adsorbed onto the substrate and the maximum water-solubility of the carrier at the dyeing temperature (80°C) used. The observed decrease in dye uptake found for concentrations of benzyl alcohol in excess of 60 g/litre can be attributed to a decrease in uptake of the carrier by the fibre and the concomitant decrease in T_g reduction, this behaviour being displayed in Fig. 5. The finding that maximum enhancement of uptake of CI Basic Blue 3 corresponded to the maximum solubility of benzyl alcohol at the dyeing temperature used agrees with those of Kim¹² for the uptake of various cationic dyes onto Courtelle S and also of Aitken *et al.* for the adsorption of CI Basic Blue 45 onto Courtelle S.

Figure 5 shows the relationship between dye and carrier uptake by the fibre, the gradient of the plot being indicative of the carrier's efficacy, in so far as the higher gradient of the line denotes the greater efficiency of the carrier in enhancing dye uptake.

The gradient of the linear relationship obtained between the extent of dye uptake and reduction in T_g of the wet fibre (Fig. 6) is important since, if its value is the same for all carriers, then it can be concluded that plasticization is the only factor that determines carrier action and that carrier efficiency is

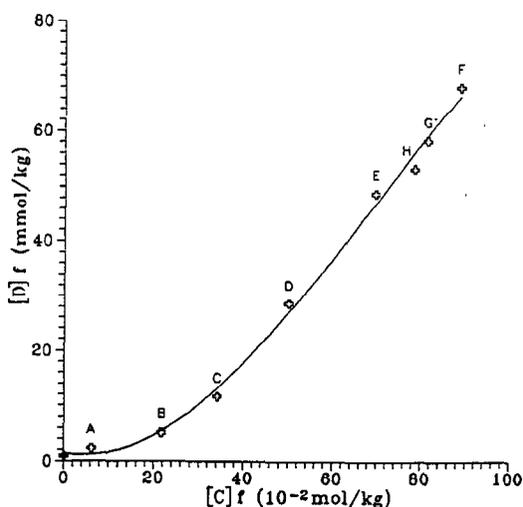


Fig. 5. Relationship between dye and carrier uptake.

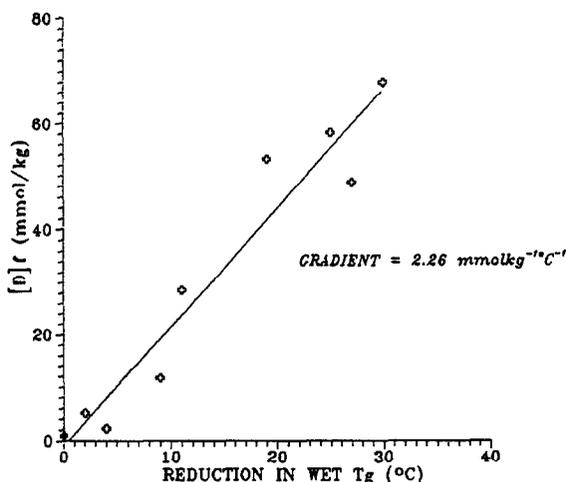


Fig. 6. The relationship between plasticization and dye uptake.

therefore determined solely by the amount of carrier adsorbed by the fibre. However, if the value of this gradient differs for different carriers, then other factors, such as the dye's solubility in the carrier, will also contribute to carrier action; this aspect of carrier action is being studied.

4 CONCLUSION

The extent of plasticization of Courtele S tow imparted by benzyl alcohol has been shown, by using dynamic mechanical analysis, to depend on the concentration of the carrier adsorbed by the fibre; the maximum extent of reduction in wet T_g (i.e. plasticization) of the acrylic fibre corresponds to the maximum uptake of benzyl alcohol by the fibre, which, in turn, corresponds to the aqueous solubility of the carrier at the particular temperature (80°C) employed. The extent of enhancement of uptake of CI Basic Blue 3 imparted by benzyl alcohol is proportional to the amount of carrier adsorbed by the fibre and thus to the extent of plasticization of the fibre caused by benzyl alcohol. The results clearly demonstrate that benzyl alcohol functions as a diluent of the fibre, facilitating dye diffusion by disruption of the structure of the fibre.

ACKNOWLEDGEMENTS

The authors wish to thank the SERC and Courtaulds Research, Spondon for provision of a scholarship to Mr Aitken, Messrs J. Catherall and R. Cox

of Courtaulds Fibres for helpful discussion and Mr K. Divan of the Department of Colour Chemistry and Dyeing for the gas chromatographic analysis.

REFERENCES

1. Takaoka, A. & Aki, M., *Sen'i Gakkaishi*, **21** (1965) 425.
2. Gur-Arieh, Z. & Ingamells, W., *J. Soc. Dyers Col.*, **90** (1974) 8, 12.
3. Gur-Arieh, Z., Ingamells, W. & Peters, R. H., *J. Polym. Sci.*, **20** (1976) 41.
4. Gur-Arieh, Z., Ingamells, W. & Peters, R. H., *J. Soc. Dyers Col.*, **92** (1976) 332.
5. Asquith, R. S., Blair, H. S. & Spence, N., *J. Soc. Dyers Col.*, **94** (1978) 49.
6. Longo, M. L., Sciotto, D. & Torre, M., *Amer. Dyest. Rep.*, **70**(7) (1981) 24.
7. Peters, R. H. & Wang, H., *J. Soc. Dyers Col.*, **98** (1982) 432.
8. Alberti, G., *Amer. Dyest. Rep.*, **72** (1983) 46.
9. Alberti, G., Cerniani, A. & De Giorgi, M. R., *Ann. Chim.*, **74** (1984) 429.
10. Alberti, G., De Giorgi, M. R. & Sen, G., *Ann. Chim.*, **74** (1984) 421.
11. Alberti, G. & Loi, A., *Melliand Textil. Ber.*, **70** (1989) 365.
12. Kim, J. P., Ph.D. Thesis, University of Leeds, 1990.
13. Aitken, D., Burkinshaw, S. M., Catherall, J., Cox, R., Litchfield, R. E., Todd, N. G. & Price, D. M., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, No. 47 (1991) 263.
14. Butler, R. H., Prevorsek, D. C. & Reimschuessel, H. K., *J. Polym. Sci., A-2*, **9** (1971) 867.
15. Reimschuessel, H. K., *J. Polym. Sci., Polym. Chem. Edn*, **16** (1978) 1229.
16. Smith, E. G., *Polymer*, **17** (1976) 761.
17. Kettle, G. J., *Polymer*, **18** (1977) 742.
18. Buchanan, D. R. & Walters, J. P., *Text. Res. J.*, **47** (1977) 398, 491.
19. Challa, G. & Tan, Y. Y., *Polymer*, **17** (1976) 7.
20. Fuzek, J. F., In 'Waters in Polymers', ACS Symposium Series, No. 127, 515 (1980).
21. Litchfield, R. E., Todd, N. G. & Price, D. M., In First International Conference on The Thermal Characterization of Polymers, Windermere, Bradford University, 1990.
22. Aitken, D., Burkinshaw, S. M., Catherall, J., Cox, R. & Price, D. M., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, No. 47 (1991) 271.