Acknowledgements

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Polarization of excimer emission in solution

J. R. MacCallum
Chemistry Department, University of St. Andrews, Fife, Scotland, UK

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Polarization of fluorescent emission of excimer structures for polystyrene and poly (α-methyl styrene) has been examined in cyclohexane solution. No depolarization was observed resulting in the conclusion that energy migration does not take place under the experimental conditions studied.

Keywords Optical properties; polarization; excimer; fluorescence; energy transfer

Introduction

Observation of polarized emission from excimer structures in thin films of polystyrene at room temperature led to the conclusion that either energy migration was not an efficient process or, if it were, the migrating exciton was retaining spatial identity as it moved into the excimer traps[1]. Provided they are aligned such that their transition moments interact with the incident radiation all phenyl units have an equal probability of excitation and consequently each step in the migration process, including the final transfer into the excimer structure, would proceed under strict control of orientation of chromophores. None of the accepted theories of energy transfer have been shown to impose such strict conditions of orientation of transition moments. In order to extend the investigation of the photophysical behaviour of poly(vinyl arenes)[2] polarization measurements have been made on solutions of both polystyrene and poly(α-methyl styrene). Under such conditions anisotropy or orientation of the macromolecules can be discounted.

Experimental

The polymers were prepared by anionic polymerization using purified monomers. Molecular weights, measured viscometrically were: polystyrene 1.2×10^5, and poly (α-methyl styrene), 8×10^4. Freshly distilled cyclohexane was used as solvent and measurements were made over a range of temperatures. De-oxygenated solutions, 10^{-2}M in repeat unit, were examined using a Perkin Elmer MPF2 with polarizers supplied by the instrument makers. The usual correction was applied for anisotropy of the optics of the instrument. The results are shown in *Table 1*.

Discussion

The fluorescent emission of excimer for both polystyrene and poly(α-methyl styrene) is polarized in solution as well as in the solid state. The solvent chosen, cyclohexane, is a poor solvent for both polymers and consequently the interphenyl separation in the macromolecules will be minimized. Such a condition should favour inter unit energy transfer. Orientation of chromophores and anisotropy of the samples, conditions which can be realized for solid solutions, cannot be relevant factors for observations made on solutions of the polymers, therefore it must be concluded that for these two polymers formation of the excimer involves the phenyl unit which makes the initial photon capture and very little energy migration takes place. Furthermore the resultant excimer structure undergoes no spatial relaxation during its life-time of approximately 20 ns. Such a situation is surprising since the excimer involves

Table 1 Polarization of excimer emission for solutions of polystyrene and poly(α-methyl styrene). Excitation – 265 nm, emission – 330 nm

Polymer	Polarization	Temperature
Polystyrene (film)	0.20	295K
Poly(α-methyl styrene) (film)	0.25	295K
Polystyrene (solution)	0.22	295K
Poly(α-methyl styrene) (solution)	0.19	308K
"	0.21	311K
"	0.21	314K
"	0.22	317K
"	0.23	320K
"	0.22	323K
"	0.23	329K

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two monomer units and relaxation of such a bulky structure by main chain bond rotation would be expected to be similar to the relaxation time for backbone bond rotation, that is approximately 5 ns. It may be that the relaxation process for the co-operative motion resulting in spatial re-orientation of the excimer is sterically unfavourable.

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Preparation of high-modulus nylon-6 fibre by an improved zone-annealing method

Toshio Kunugi
Department of Applied Chemistry, Faculty of Engineering, Yamanashi University, Kofu-shi, 400
Japan

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We have prepared high modulus, high strength nylon-6 fibres from crystalline polymers by an annealing method called 'zone-annealing'. In this study the zone-drawing was repeated 4 times (heater temperature 80°C; heater moving speed 40 mm min^{-1}; under tension of 1.6 kg mm^{-2}). Zone-annealing conditions were decided after numerous preliminary experiments. It was thought that the amorphous molecular chains become selectively loose when the tension is removed after zone-annealing and relaxation leads to a decrease in macro-modulus. This was prevented by heat-setting on the zone-drawn and zone-annealed nylon-6 fibre.

Keywords Heat treatment; mechanical properties; nylon-6 fibre; annealing; stability; modulus

Introduction

We have succeeded in preparing high-modulus and high-strength fibres from crystalline polymers, already widely used, by a new annealing method called the 'Zone-annealing Method'. So far this method has been applied to poly(ethylene terephthalate)[1-6], polyethylene[1-3,7], and nylon-6[1-4,8,9]. In spite of very simple apparatus and easy procedure, the resulting fibres exhibited excellent mechanical properties and high dimensional stabilities at elevated temperatures.

In the case of nylon-6, however, the extent of approach of the maximum modulus to the crystal modulus (6.5%) is markedly low compared with those of poly(ethylene terephthalate) (19.8%) and polyethylene (23.0%). This indicates that there is room for further improvement of the mechanical properties. With the intention of investigating this point, we have attempted an improved zone-annealing method and a subsequent heat-setting. Consequently, we could obtain a fibre with a remarkably high modulus.

Experimental

The original material used in this study is as-spun nylon-6 fibre of diameter, 0.41 mm, supplied by Toray Research Center, Inc. The fibre has a birefringence of 9.5×10^{-4}, a crystallinity of 29.4% and $\bar{M}_n = 2.86 \times 10^4$, $\bar{M}_w = 1.18 \times 10^5$. The apparatus used for zone-drawing and zone-annealing is identical to that used in the previous studies[1-9]. The procedure consists of two stages: namely zone-drawing and zone-annealing. The zone-drawing was repeated 4 times increasing the tension applied to the fibre from 0.90 to 18.4 kg mm^{-2} at a band-heater temperature of 80°C with a heater moving speed of 40 mm min^{-1}. The zone-annealing was carried out 6 times under a tension of 21.5 kg mm^{-2} at a band-heater temperature of 180°C with a moving speed of 300 mm min^{-1}. Subsequently the zone-drawn and zone-annealed fibre was heat-set. Heat-setting was carried out at 190°–200°C for 5 min under a nitrogen gas atmosphere. The dynamic viscoelastic properties, E', E'', tan δ were measured at 110 Hz over a temperature range from room temperature to 190°C at a heating rate of 1.5°C min^{-1}.

Results and Discussion

As nylon-6 crystallizes easily on cooling from the molten state and during storage in atmospheric moisture, even as-spun fibre has a large number of lamellae. In order to further increase the modulus, it is necessary to more effectively unfold the lamellae and to form a more-extended chain structure. The zone-drawing in the previous studies[8,9] was carried out only once at a band-heater temperature of 80°C with a heater moving speed of 40 mm min^{-1} under a tension of 1.6 kg mm^{-2}. However, in the present study the zone-drawing was repeated 4 times under the conditions described above. The conditions for zone-annealing were also decided after numerous preliminary experiments. It is considered that the amorphous molecular chains become selectively loose when the tension is removed after zone-annealing and the relaxation leads to a decrease in macro-modulus. To prevent the unfavourable relaxation of amorphous molecular chains, heat-setting was subsequently attempted on the zone-drawn and zone-annealed fibre.

Figure 1 shows the temperature dependence of dynamic storage modulus for the three kinds of the fibres. It is clear from the figure that the fibre prepared by the improved zone-annealing method is far superior to one by

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