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Elucidation of the hard segment transition in a diacetylene-containing copolyurethane using modulated differential scanning calorimetry

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A segmented copolyurethane containing diacetylene units in the hard segments has been analysed using modulated differential scanning calorimetry (m.d.s.c.). An endothermic peak is observed in the m.d.s.c. reversible heat flow curve at about 160°C which is due to an order–disorder transition of the paracrystalline diacetylene-containing hard segments. Such a transition is confirmed for the first time, since it was undetectable in previous conventional d.s.c. analysis. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: segmented copolyurethanes; diacetylene; hard segments; order–disorder transition)

Introduction

In previous reports[1,2], extensive discussion was carried out on the synthesis, structure and opto-mechanical properties of glassy diacetylene-containing segmented copolyurethanes. Upon thermal treatment, diacetylene units in the hard segments of the copolymer cross-polymerize into polydiacetylene chains via a solid state topochemical reaction similar to that which occurs in diacetylene single crystals. Such conjugated polydiacetylene chains not only provide chemical cross-linking and mechanical reinforcement in the hard segments but also give the copolyurethanes their unique optical properties. Such copolymers were characterized systematically using conventional d.s.c., dynamic mechanical analysis, X-ray diffraction and transmission electron microscopy (TEM). The findings have led to the proposition of a supramolecular structure for the diacetylene-containing hard segments. Although it has been speculated that the hard segments might undergo an order–disorder transition, the understanding of the solid state reaction and relaxation inside the paracrystalline hard segments of these copolymers is far from comprehensive. Furthermore, there is no direct evidence showing the transition in the diacetylene-containing hard segments and its effects on the solid state polymerization. Thus, this work is undertaken to reveal the details of the reactions and transitions in the diacetylene-containing supermolecular hard segments of the copolyurethane. Characterization by using modulated d.s.c. (m.d.s.c.) indicates, along with other thermal activities, an endothermic transition of the paracrystalline hard segments which was undetectable by the conventional d.s.c. analysis.

Experimental

Samples of the diacetylene-containing copolyurethane, based on 47.8% 4,4′-diisocyanodiphenylmethane, 10.4% hexadiyne-diol and 41.8% of a polypropylene glycol ($M_n = 400\,\mathrm{g\,mol^{-1}}$), were synthesized using a previously described method[1]. The number-average molar mass of the copolymer was determined as $10\,600\,\mathrm{g\,mol^{-1}}$ using gel permeation chromatography. Partially cross-polymerized samples were obtained via post-heat treatment of the as-prepared copolymer at 100°C for 40 h. The material was analysed using a modulated differential scanning calorimeter (TA Instrument) in a constant nitrogen flow environment. The calorimeter uses a modulated sinusoidal heating/cooling schedule while keeping the average heating rate constant[3–5]. Tests were carried out at two different modulated heating rates, i.e. 2.5 and $5^\circ\mathrm{C\,min^{-1}}$. The amplitude of the heating rate modulation was ± 1°C, and the period was set at 60 s. The effects of post-heat treatment on the thermal properties were also studied.

Results and discussion

In an m.d.s.c. analysis, the modulated heating rate has the effect of heating and cooling the sample, and in so doing the technique allows the total heat flow signal be deconvoluted into two parts, i.e. non-reversible heat flow (out of phase with the sinusoidal heating schedule) and reversible heat flow (in phase with the sinusoidal heating schedule)[3,4]. One of the advantages of m.d.s.c. is its ability to discern mixed thermal activities which occur over the same temperature range that would otherwise not be separable using conventional d.s.c. A set of m.d.s.c. traces, which include the total, reversible and non-reversible heat flow curves, of the as-prepared copolymer tested at a heating rate of $2.5^\circ\mathrm{C\,min^{-1}}$ are presented in *Figure 1*. A better defined glass transition was observed from the reversible heat flow curve than that from the total heat flow curve. It is useful to point out that the total heat flow is what would be detected using conventional d.s.c. On the other hand, T_g is

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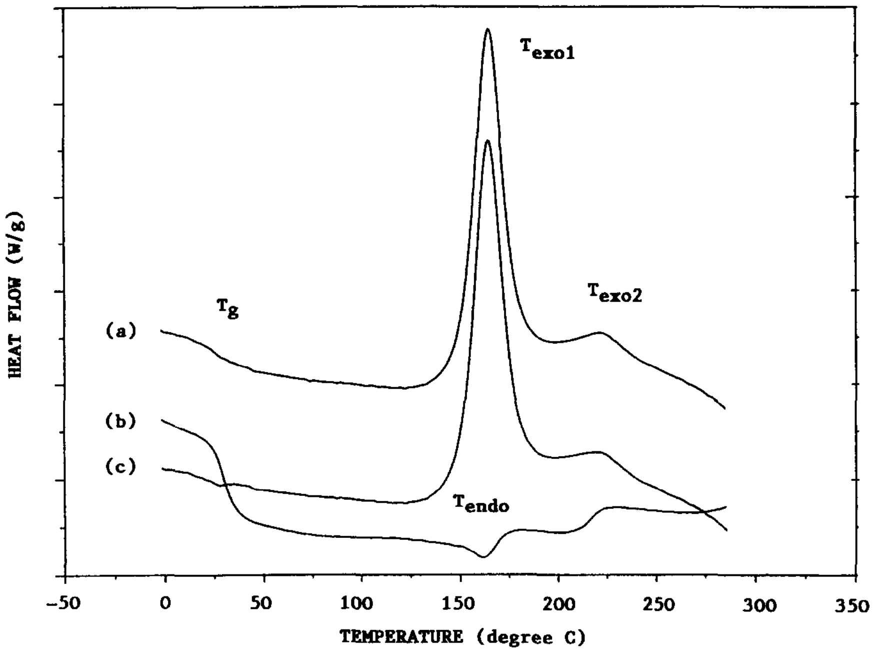

Figure 1 M.d.s.c. curves of the as-prepared diacetylene-containing segmented copolyurethanes tested at 2.5°C min^{-1} with 1°C/60 s modulation: (a) total heat flow; (b) reversible heat flow and (c) non-reversible heat flow

absent in the non-reversible heat flow curve since a glass transition is a reversible thermal phenomenon. However, a small endothermic transition appears instead in the non-reversible heat flow curve, and may be ascribed to the relaxation of some kind of stress at T_g, which sometimes causes an 'over-shot' glass transition in the conventional d.s.c. heat flow curve. The large exothermic transition of the solid state cross-polymerization of the diacetylene units at 165°C (T_{exo1}) appears in both the total and non-reversible heat flow curve, as the thermally induced cross-polymerization is non-reversible. However, it is most interesting to find, from the reversible heat flow curve, that an endothermic transition occurs between 120 and 180°C and peaks at 161°C (T_{endo}), which can be attributed to the order–disorder transition of the diacetylene-containing hard segment supermolecular structures. Also, this endothermic peak temperature is only a few degrees lower than that of the main peak of the exothermic reaction. Hence it is not unexpected that the endothermic transition was absent from the conventional d.s.c. analysis of the copolymer because it was masked completely by the intense exothermic transition from the cross-polymerization of the diacetylene units. The weak endothermic transition detected in the m.d.s.c. reversible heat flow curve agrees well with previous observations of the spherulite-like, paracrystalline nature of the hard segment aggregates from the X-ray and TEM analysis. Now it is also possible to confirm that the previously reported[1] drop of the storage modulus (E') from 120 to 150°C in the d.m.t.a. temperature scan curve is due to the molecular movement in the hard segments. Since the endothermic order–disorder transition immediately precedes the large exothermic reaction, it suggests that this transition may have facilitated the cross-polymerization process via reorganization of the arrays of diacetylene monomer units into structures that are more favourable for the solid state polymerization to take place. More detailed work is being carried out on the kinetics of the thermally induced cross-polymerization reaction. Also observed in the reversible heat flow curve is an exothermic step transition at about 200°C. In fact there is a significant difference between the heat flow value prior to the large exothermic peak at 120°C and that after the exothermic peak at 240°C. This does not seem to be due to the baseline drift of the instrument. Rather, the change in heat capacity of the materials is most likely responsible for this phenomenon as the diacetylene monomers in the hard segments cross-polymerize into conjugated polydiacetylene chains, which are of high stiffness, through the exothermic reaction. The resulting chemical cross-linking and molecular stiffening effects would thus cause an

Table 1 Summary of the m.d.s.c. data of the diacetylene-containing copolyurethane

Heating rate (°C min^{-1})	T_g (°C)	T_{exo1} [a] (°C)	ΔH_{exo1} [a] (J g^{-1})	T_{exo2} [a] (°C)	T_{endo} [b] (°C)	ΔH_{endo} [b] (J g^{-1})
2.5	24.3	164.7	162.0	222	161.3	4.6
5	25.8	173.3	154.0	233	167.0	5.2
2.5[c]	41.4	177.2	50.0	221	164.5	0.9

[a] Data obtained from total heat flow curves
[b] Data obtained from reversible heat flow curves
[c] Post-heat treated sample

increasing restraint for the molecular movement in the hard segment aggregates, which in turn gives rise to the apparent 'inverse' glass transition, i.e. the exothermic step transition. This observation corresponds well to the increase in the storage modulus (E') above 150°C found previously in the copolymers[1]. Similar m.d.s.c. curves are obtained when the tests were carried out at $5^{\circ}\mathrm{C\,min}^{-1}$ or with post-heat treated samples. All data obtained on the reactions, transitions or relaxations in the copolymers are summarized in *Table 1*. The effects of heating rate and post-heat treatment of the as-prepared samples are generally as expected. One point worth noting is that the endothermic transition diminishes and shifts to higher temperature after post-heat treatment since the substantial cross-polymerization results in cross-linking. It is also interesting to note that there is a second, weaker, exothermic peak or shoulder in both the total and non-reversible heat flow curves whose peak temperature (T_{exo2}) increases with heating rate but which is unaffected by post-heat treatment. This second peak is more likely to be due to certain degradation reactions of the urethane part of the copolymer.

Conclusion

M.d.s.c. results indicate an endothermic transition immediately prior to the exothermic transition of the cross-polymerization. This is ascribed to the order–disorder transition of the paracrystalline diacetylene-containing hard segment supramolecular structures of the copolyurethane. The endothermic transition, undetectable using conventional d.s.c. analysis, is found to diminish and shift to higher temperature upon cross-polymerization as the hard segment aggregates become cross-linked. The results shown are in good agreement with those observed previously from dynamic mechanical thermal analysis, X-ray diffraction and TEM.

Acknowledgements

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