Formation and properties of urethane–diacetylene segmented block copolymers

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Two types of urethane–diacetylene segmented block copolymers have been prepared using a one-step bulk polymerization process. By varying the length of the polyether soft segments using different polyols, copolymers with different physical properties have been produced. In one case a copolymer which is rubbery at room temperature has been prepared by using a polyoxypropylene diol with a molecular weight of 1000 g mol^{-1}. The other material obtained using a polyoxypropylene diol with a molecular weight of 400 g mol^{-1} is glassy at room temperature. It has been found that the phase-separated hard domains will undergo thermally induced, solid-state cross-polymerization of the diacetylene groups in the domains. This is found to lead to a modification of the physical properties of the materials involving a change in colour, and an increase in the thermal stability, glass transition temperatures and the Young's moduli of the copolymers. The mechanical properties of the polymers have been interpreted using the Takayanagi mechanical models and the average modulus of the cross-polymerized hard segments has been determined to be about 5 GPa. Well-defined Raman spectra characteristic of conventional polymers have been obtained from the copolymers and it is found that the position of the Raman bands shifts to lower frequency during tensile deformation. This is shown to be due to deformation taking place within the hard segments and it is demonstrated that Raman spectroscopy offers a unique way of determining hard segment deformations in these materials.

(Keywords: copolyurethanes; polydiacetylenes; segmented block copolymers; Raman spectroscopy; deformation; thermal behaviour)

INTRODUCTION

Segmented copolyurethanes are characterized by a two-phase morphological structure comprising incompatible rigid, glassy hard segments (HS) and extensible, rubbery soft segments (SS). The detailed morphology depends primarily on the relative proportions of HS and SS: at low HS contents, the rubbery SS form the continuous phase in which dispersed HS domains act essentially as a reinforcing filler and multifunctional crosslinks[1]. At high HS contents, phase inversion can occur and the copolyurethane may be regarded as a rubber-toughened plastic in which the HS form the continuous phase and the SS are dispersed rubber particles. Seldom is phase separation complete, particularly in copolyurethanes in which appreciable hydrogen bonding between HS and SS occurs[2]. Consequently, the transition from one morphology to the other is not sharp and at intermediate HS contents, the copolymer may comprise a bi-continuous and interpenetrating, two-phase structure.

The nature of the morphological structure largely determines the properties of segmented copolyurethanes. The mechanical properties in particular depend not only on HS content but also on HS domain size, the cohesive strength of the domains and their ability to orient in the direction of an applied deformation: the deformation behaviour of the SS phase also affects copolymer properties, but to a lesser extent[2]. Clearly, for a segmented copolyurethane subjected to deformation, the distributions of stress and strain between HS and SS phases will be different. Attempts[3,4] have been made using infra-red dichroism to investigate the response of HS in copolyurethanes subjected to low and high strains, but the results yielded only information concerning HS orientation. A more specific analytical technique is therefore necessary to study the detailed deformation behaviour within an individual phase. It then follows that the chemical and topological structure of the phase must be well-defined and quantitatively responsive to the technique employed.

Previous studies[5–7] have shown that phase-separated copolymers containing highly spectroscopically active HS phases based on cross-polymerized polydiacetylenes, can be formed under controlled synthesis conditions. In particular, copolyurethanes comprising SS based on a polyoxytetramethylene diol ($M_n = 1000$ g mol^{-1}) and HS formed from either hexamethylene diisocyanate (HDI) or 4,4′-methylenediphenylene diisocyanate (MDI) reacted with either 2,4-hexadiyne-1,6 diol (HDD) or 5,7-dodecadiyne-1,12 diol (DDD), were shown after controlled cross-polymerization to give strong Raman spectra[7]. Hard segment contents were in the range 19–24 w/w% and cross-polymerization was effected to varying degrees by thermal and γ-radiation treatments. The use of Raman spectroscopy was limited to characterizing only undeformed copolyurethanes to demonstrate the presence of conjugated polydiacetylene moieties within HS phases, in relation to the detailed chemical structure of the HS repeat units.

Raman spectroscopy however, has been used much

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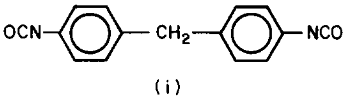
more effectively to yield quantitative information on the deformation of substituted polydiacetylene, single-crystal fibres[8–10]. These studies have shown that well-defined resonance Raman spectra can be obtained from single crystal fibres of substituted polydiacetylenes. When the fibres are subject to deformation, the position of the bands in the Raman spectrum are found to shift to lower frequency with the largest shift being for the –C≡C– triple bond stretching band which moves by about 20 cm^{-1} for 1% applied strain in single crystals. This shift is a reflection of the macroscopic deformation directly deforming the covalent bonds along the polymer backbone. As well as giving an important insight into molecular deformation in a polymer single crystal, the phenomenon can be employed to follow the micromechanics of deformation of fibres within a composite[10]. For example, it has been possible to map the distribution of strain along a polydiacetylene fibre in a model composite consisting of a single fibre embedded in an epoxy resin bar and to determine parameters such as the critical length as a function of fibre diameter[10]. Recent studies have shown this Raman strain measurement technique to be applicable to a wide variety of fibre and composite systems[11–15]. However, until this present study, strain measurements have been confined to the fibres rather than the matrix.

This paper presents results of studies on the structure–property relations in segmented copolyurethanes comprising completely amorphous SS, based on polyoxypropylene (PPG) diols, and thermally cross-polymerized polydiacetylene HS formed from MDI and HDD. Specifically, the distributions of localized stress and strain within HS phases have been measured using Raman spectroscopy applied to the copolyurethanes subjected to simultaneous tensile deformation.

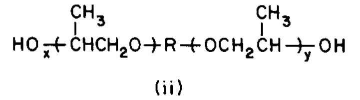
EXPERIMENTAL

Synthesis, purification and characterization of reactants

Two linear polyurethanes (PUs), with glass transition temperatures (T_gs) of −28 and 26°C (by differential scanning calorimetry, d.s.c.), were used as the continuous, SS matrix materials in the molecular composites. The PUs were formed from reactants whose chemical structures are shown below, namely, pure MDI (i) and each of two polyoxypropylene diols (ii), PPG 1000 and PPG 400, for which $(x+y) \approx 16$ and 6, respectively. In the segmented copolyurethanes, the discontinuous, reinforcing phase comprised rigid HS formed from MDI and the low molar mass, diol chain extender (iii), 2,4-hexadiyne-1,6 diol, HDD.



(i)



$$HO_x\left(\overset{CH_3}{\overset{|}{C}}HCH_2O\right)R\left(OCH_2\overset{CH_3}{\overset{|}{C}}H\right)_y OH$$

(ii)

$HOCH_2C{\equiv}C{-}C{\equiv}CCH_2OH$

(iii)

4,4′-Methylenediphenylene diisocyanate, MDI (ex. BDH). The aromatic MDI, in flake form, was melted and filtered through a grade 4 sinter (50°C) using a Buchner flask and water pump (10 mm Hg). The equivalent weight of the MDI was determined to be 125 g mol^{-1} by –NCO titration.

Polyoxypropylene diols, PPG 400 and PPG 1000 (ex. BDH). Both diol pre-polymers were dried by vacuum rotary film evaporation (100°C/0.3 mm Hg) for 5 h. Characterization was carried out using end-group acetylation[16] to give equivalent weights (that is, molar masses per functional group) of 203 and 498 g mol^{-1}, respectively, for PPG 400 and PPG 1000.

2,4-Hexadiyne-1,6 diol, HDD. This reactant was synthesized from propargyl alcohol (ex. Fluka Chemicals) according to the procedure reported by Hay[17], and was recrystallized from boiling toluene (111°C) and vacuum dried (90°C/4 h) prior to use. The pure HDD was obtained as fine white crystals and had a melting point of 112°C (lit. 109–113°C).

Synthesis of polyurethane matrices and polyurethane–diacetylene copolymers

The two linear PUs (isolated SS homopolymers formed from MDI and each PPG) and the corresponding PU–diacetylene copolymers were all formed in bulk, using a one-step polymerization process to simulate industrial processes such as reaction injection moulding (RIM).

The rapid development of RIM has resulted in significant increases in the productions of PU materials, particularly segmented copolyurethane elastomers. The formation of such elastomers by RIM is by definition a one-step, bulk copolymerization process[18] in which one reactant stream comprises a blend of polyether prepolymer and diol chain extender and the other reactant stream is a liquefied form of MDI. In this context, the urethane–diacetylene segmented copolymers studied here were formed by a hand-casting technique involving a similar one-step, bulk (rather than solution) copolymerization process which therefore overcomes the subsequent need to remove solvent. This process is in distinct contrast to the multi-step, solution method employed by other workers[5–7] and provides an interesting comparison in terms of the structures and properties of the copolymers produced. In the bulk process, a significant rise in temperature due to the polymerization exotherm is inevitable and some cross-polymerization of the diacetylene-based HS will always occur, which is not the case in the solution process. In addition, the one-step process enables HS of greater length to form although the distribution of HS lengths is broader than in the multi-step process. Consequently, in the phase-separated copolyurethane, the HS domains are less well-defined and are more easily disrupted when subjected to temperature and deformation.

In the present studies, urethane homopolymers and copolymers were formed using a single-step or one-shot process[19]. In all cases, polymerizations were carried out without catalysts using an overall stoichiometric ratio, r, of unity and an initial reaction temperature of 80 ± 1°C. Formulations, based on the different proportions by weight of reactants used to form the various polymers, are given in *Table 1*.

Table 1 Relative parts by weight of reactants used to form various homopolyurethanes and urethane–diacetylene copolymers

	Material				
Reactant	PPG1000/MDI	PPG1000/HDD/MDI	PPG400/MDI	PPG400/HDD/MDI	HDD/MDI
MDI	1.00	1.00	1.00	1.00	1.00
HDD	–	0.22	–	0.22	0.44
PPG1000	3.87	1.99	–	–	–
PPG400	–	–	1.60	0.81	–

Typically, between 50 g and 100 g of total reactants were used in formulations. In the segmented copolyurethanes, the molar ratios of reactants were PPG:HDD:MDI ≡ 1:1:2 and the weight percentages of diacetylene-based HS in PPG 1000/HDD/MDI and PPG 400/HDD/MDI were 22.4 and 35.5, respectively. Hard segment content is defined as the mass of HDD plus the stoichiometric equivalent of MDI divided by the total mass of the formulation. In a typical preparation, the PPG diol and the stoichiometric equivalent amount of HDD were weighed accurately into a 250 ml sealed flanged reaction vessel, equipped with a stirrer, and immersed in a thermostatted water bath (80 ± 1°C). The pale yellow reaction mixture was stirred and de-gassed by applying vacuum (~0.3 mm Hg). (In the case of homopolyurethanes, HDD was omitted.) The stoichiometric equivalent amount of molten MDI was then added to the polyol blend via a heated glass funnel. The complete reaction mixture was stirred continuously for 2 h at 80°C (although the initial reaction exotherm raised the temperature to ~120°C for a few minutes). During the reaction time, the initial clear mixture became cloudy as the polymerizing diacetylene–urethane HS and polyether–urethane SS phase separated: there was also a colour change from pale yellow to deep orange–brown and an increase in viscosity as the overall molar mass increased. After the 2 h period, vacuum was re-applied to de-gas the reaction mixture which was cast into picture-frame moulds, previously sprayed with silicone release agent and pre-heated to 80°C. (Some of the reaction mixture, which became semi-solid at room temperature, was kept for subsequent thermal analysis by d.s.c.). Polymerization of the reaction mixtures was then completed by subjecting the cast materials to a curing schedule of 120°C for 36 h. There was a further colour change during curing to deep purple, and d.s.c. experiments showed that no further reaction could be achieved. The cured copolyurethanes were stored in a vacuum desiccator containing silica-gel until subsequent testing. (The homopolyurethane SS materials, PPG 1000/MDI (an elastomer) and PPG 400/MDI (a soft, ductile plastic), were transparent, pale yellow materials: that is, no colour changes occurred during preparation and curing.)

Synthesis of homopolyurethane HS, HDD/MDI

In contrast to the homopolyurethane SS, PPG 1000/MDI and PPG 400/MDI, and the corresponding diacetylene–urethane copolymers, which were all formed in bulk, the homopolyurethane HS material, HDD/MDI, could only be formed in solution. As shown in *Table 1*, HDD/MDI was synthesized from stoichiometric equivalent amounts of pure HDD and MDI in freshly distilled dimethylformamide (DMF) solution. The HDD (~15 g) was weighed accurately into a 50 ml flanged reaction vessel to which DMF (7.5 ml) was added to dissolve fully the HDD at 21°C. The sealed reaction vessel was fitted with a mechanical stirrer and then immersed in a glass-sided, thermostatted water bath at 40 ± 1°C. The HDD solution was stirred and de-gassed simultaneously (~0.3 mm Hg) by means of a rotary vacuum pump. The required amount (~35 g) of MDI was accurately weighed and added to the HDD solution via a warmed glass funnel, and the total reaction mixture was stirred and de-gassed for 2 min. Initially, the HDD/MDI/DMF reaction mixture was a clear, pale yellow colour and during the 2 min period, the reaction mixture became progressively cloudier as phase separation between polymer and DMF solvent occurred. After 2 min, the reaction exotherm had increased the temperature to ~150°C and the cloudy reaction mixture became orange–brown in colour. The partially polymerized mixture was poured into a pre-heated (80°C) picture-frame mould which was placed in an oven for 6 h at 120°C at atmospheric pressure and then in a vacuum oven at 120°C for a further 30 h to effect complete reaction and to remove all the DMF. After the first 6 h at 120°C, the sample turned dark brown, and after complete reaction (36 h) the HS homopolyurethane was a deep brown–purple colour.

Materials characterization

Homopolyurethanes and urethane–diacetylene copolymers were characterized in terms of their thermal, dynamic-mechanical and tensile properties using the following techniques.

Differential scanning calorimetry measurements were made on a Dupont 990 thermal analyser equipped with a d.s.c. cell. Samples (~10 mg) and an inert reference material, glass beads (~10 mg) were encapsulated in aluminium pans and cooled to −120°C in the cell which was then heated in air at 20°C min^{-1} to 280°C. Glass transition temperatures were determined from d.s.c. traces: d.s.c. traces were also used to assess the degradation behaviour of materials.

Dynamic mechanical thermal analysis (*d.m.t.a.*) was carried out on a Polymer Laboratories apparatus operating at a frequency of 1 Hz in the temperature range −150 to 200°C at a heating rate of 5°C min^{-1}. A double-cantilever bending geometry was used for beam samples (3 × 10 × 45 mm) to obtain dynamic flexural moduli (E') and mechanical damping factors (tan δ) as functions of temperature.

Tensile properties (*ASTM D638M-81*) were determined from the mean of at least five stress–strain experiments carried out at 23°C on an Instron 1122 universal testing machine. Dumb-bell specimens were deformed to fracture at an extension rate of 5 mm min^{-1}, and tensile strains were determined accurately and independently of stress measurements using a 10% strain gauge extensometer.

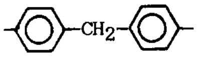
In addition, a detailed investigation of the micromechanics of deformation of the copolyurethanes was carried out using a specially modified Raman spectroscopy technique.

RESULTS AND DISCUSSION

Chemical structure

The homopolyurethane SS, PPG 1000/MDI and PPG 400/MDI, are linear amorphous materials which at room temperature are, respectively, a soft elastomer and a 'leathery', ductile plastic. The homopolyurethane HS, HDD/MDI, after cross-polymerization (see later), is a highly crosslinked material which at room temperature is a glassy but ductile plastic. In the urethane–diacetylene copolymers, which may be described as molecular composites, the degree of reinforcement of the SS attained by incorporating dispersed HS, depends on: (1) HS content (expressed as a weight percentage); (2) the degree of phase separation and connectivity between hard and soft segments; and (3) the degree of crosslinking in the HS, achieved by thermal cross-polymerization of the diacetylene moieties.

The poly(urethane–diacetylene) materials are more accurately described as segmented block copolymers of the $\text{-}(AB)_n\text{-}$ type in which the hard (A) and soft (B) segment blocks phase separate to yield a bulk material comprising a soft polyether matrix reinforced with hard glassy domains. A simplified reaction scheme showing the formation of the segmented block copolyurethanes from reactants (i) to (iii) in which –R– is



is shown in *Figure 1*. Ideally, block copolymers of structure (iv) are linear with the SS being totally amorphous and the HS having some potential for crystallization. The microstructural features, which define the morphology of such materials, are shown schematically in *Figure 2*. For PPG/HDD/MDI copolymers, the thin lines represent the polyoxypropylene SS chains and the sequences of circles and squares represent the diacetylene–MDI, HS chains. Phase separation results in aggregation of the HS into highly hydrogen-bonded, rigid domains. It should be noted that the size and orientation of domains varies, that there is a distribution of HS chain lengths and that some isolated HS are seen to be dispersed (or phase-mixed) within SS chains. As described in the introduction, diacetylene units if present in suitable aggregated form, as either crystallites or complexes, and if subjected to heat or irradiation, undergo topochemical reaction to form the polydiacetylene. In the case of the segmented copolyurethanes with the type of microstructure depicted in *Figure 2*, topochemical reaction proceeds along arrays of diacetylene units attached (or adsorbed) in a spatially, well-defined manner within rigid, hydrogen-bonded HS domains dispersed in the SS, polyether 'solution'. This type of reaction is normally referred to as matrix polymerization[20] and is clearly an appropriate description in the formation of the present materials since it implies that some information originally present in the template HS molecules and domains, such as molar mass and molar mass distribution, type and degree of stereoregularity, is transferred to the reaction product. Thus, assuming the HS block in the $\text{-}(AB)_n\text{-}$ block copolymer (iv) shown in *Figure 1* is part of a larger, phase-separated domain, then its structure is transformed by matrix polymerization according to the reaction shown in *Figure 3*. (This reaction scheme is analogous to that reported for the formation of substituted polydiacetylene single crystals[10,20], except that the substituents are now shown as continuing methylenediphenylene urethane chains.)

The topochemical, matrix polymerization causes a configurational change in specific parts of the HS and the resulting chains forming HS domains are cross-polymerized. Hard segments thus comprise two different polymer chains whose axes, relative to each other, define different spatial directions. These are depicted schematically in the simplified structure (v) with the polydiacetylene (repeat structure in curved parentheses; degree of polymerization, $DP = m$) shown as a diagonal chain with direction from top left to bottom right, and the

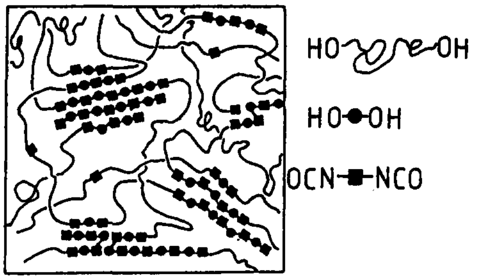
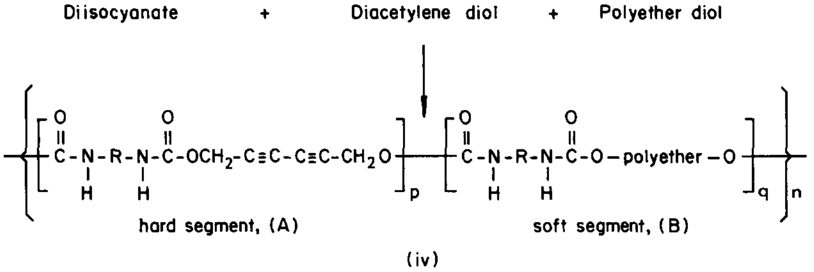


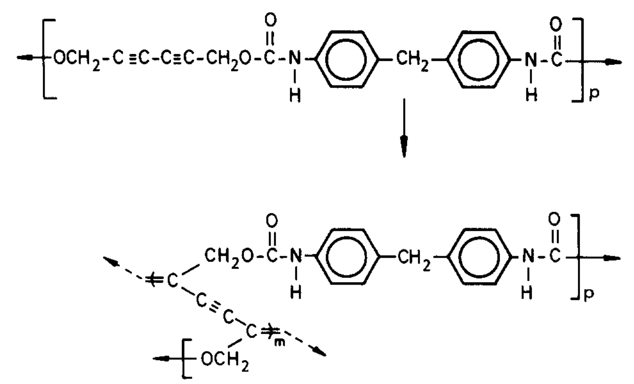
Figure 2 Schematic diagram of the major microstructural features in a segmented urethane–diacetylene copolymer



$$\left\{\left[\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-OCH_2-C{\equiv}C-C{\equiv}C-CH_2O\right]_p\left[\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-\text{polyether}-O\right]_q\right\}_n$$

(iv)

Figure 1 Schematic representation of the formation of segmented urethane–diacetylene copolymers



(v)

Figure 3 Schematic representation of the topochemical, matrix polymerization of diacetylene units to produce cross-polymerized hard segments in urethane–diacetylene copolymers

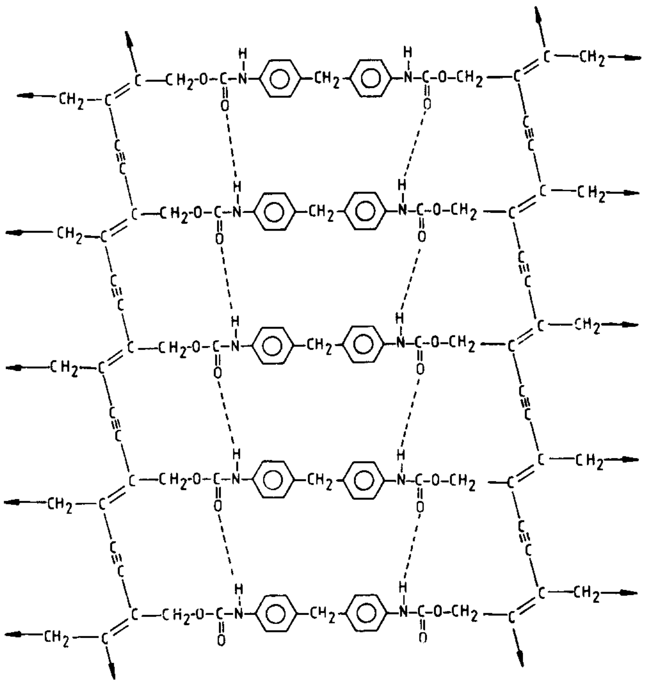


Figure 4 Idealized structure of a cross-polymerized, poly(urethane–diacetylene) HS domain showing intermolecular hydrogen bonding between neighbouring urethane groups. The diacetylene chain axis is from top-to-bottom: the methylenediphenylene–urethane chain axis from side-to-side

methylenediphenylene-based PU (repeat structure in square parentheses, $DP = p$) as a stepped, horizontal chain. The polydiacetylene chain may be regarded as a polymeric crosslink and the overall crosslink density in the HS is therefore very high. The overall, three-dimensional structure of the finally cross-polymerized HS is shown by the idealized representation in *Figure 4* which depicts the domain as a completely hydrogen-bonded, ladder polymer. The degree of crosslinking depends on the extent of cross-polymerization which for a given weight fraction of HS, is related to the average *DP*, *p*, in structure (v) and to domain size as determined by the degree of phase separation between HS and the SS matrix.

These urethane–diacetylene copolymers, therefore, are characterized by complex molecular and morphological structures, and the various processes of copolymerization, phase separation and topochemical cross-polymerization occur simultaneously to varying degrees during the materials preparation producing dramatic colour changes and intensification. This is inevitable in a one-step bulk polymerization process in which a rapid exotherm is produced.

Thermal properties: d.s.c.

Differential scanning calorimetry measurements were carried out as described earlier. Typical d.s.c. curves are shown in *Figure 5* in which curves A refer to partially reacted and lightly cross-polymerized (orange–brown coloured) materials obtained prior to curing at 120°C for 36 h. Curves B refer to completely reacted and more highly, but not fully, cross-polymerized (deep brown–purple coloured) materials. Curves C in *Figure 5a* and *b* are for the homopolyrethane SS materials, PPG 1000/MDI and PPG 400/MDI, respectively. Curve B′ in *Figure 5c* is for the homopolyurethane HS material, HDD/MDI, which has been quench-cooled from 280 to −100°C after d.s.c. measurement on the same material giving the original curve B. (For clarity, the d.s.c. curves of *Figure 5a–c* are split into left- and right-hand plots

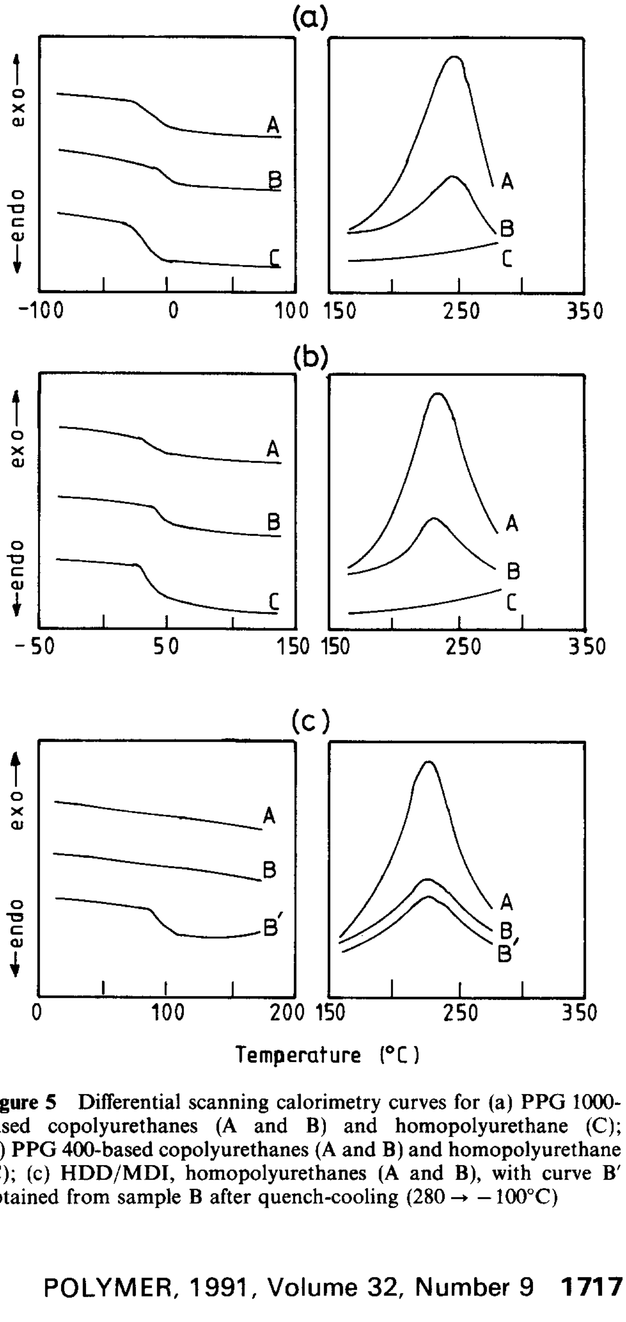


Figure 5 Differential scanning calorimetry curves for (a) PPG 1000-based copolyurethanes (A and B) and homopolyurethane (C); (b) PPG 400-based copolyurethanes (A and B) and homopolyurethane (C); (c) HDD/MDI, homopolyurethanes (A and B), with curve B′ obtained from sample B after quench-cooling (280 → −100°C)

which have identical temperature scales but different exothermic–endothermic ordinate scales, with the right-hand plots having the smaller scales.)

The homopolyurethane SS materials show only one transition as an endothermic base-line shift, resulting from a glass-to-rubber transition. The corresponding urethane–diacetylene copolymers show similar transitions but there are also pronounced exothermic peaks at much higher temperatures (>200°C) attributed to thermally induced, liquid-phase cross-polymerization[20]. In neither copolyurethane was an endothermic peak(s) observed between 50°C and 200°C which might have been expected from melting of HS crystalline domains. The absence of endothermic melting behaviour is probably due to the low molar mass and partial cross-polymerization of the HS in both uncured and cured materials. Even in the isolated, homopolyurethane HS material, no evidence of any melting endotherms was observed as shown in *Figure 5c*, or if there were, the melting temperatures coincided with and were masked by the much more intense cross-polymerization exotherms. In all cases, the intensity of and the area beneath the exothermic peaks are significantly reduced on curing the materials (120°C/36 h) showing increased cross-polymerization of the HS. However, complete cross-polymerization (or elimination of the exothermic peak) could never be achieved by thermal treatment. In separate experiments, extending the cure time to 48 h at 120°C produced no further reduction in intensity of the exothermic peak in d.s.c. traces, but did initiate thermal degradation with the material becoming friable.

An interesting feature in the d.s.c. curves of *Figure 5c* for HDD/MDI is the development of a glass transition at 85°C (in curve B′) following quench-cooling. The ladder-like, HS structure in *Figure 4* suggests molecular mobility to be severely restricted and would appear to account for the absence of a glass transition as confirmed by curves A and B. However, after quench-cooling from 280 to −100°C, the HS domain structure is disrupted and hydrogen bonding reduced sufficiently that relatively large-scale, co-operative segmental motion along chains between acetylinic crosslinks becomes possible and T_g can be observed at 85°C. The transitional behaviour derived from the various d.s.c. curves is summarized in *Table 2* in which T_g refers to the glass-transition temperature, and T_{cp} refers to the cross-polymerization temperature, determined from the peak value of the exotherm. In *Table 2*, the phase-separation ratio (PSR) is determined[21] as the heat capacity change per unit mass, $\Delta C_p/m$, at T_g for the copolyurethane relative to $\Delta C_p/m$ for the corresponding homopolyurethane SS. For complete phase separation, PSR = 100%, and for complete phase mixing, PSR = 0%.

Values of T_g for PPG 1000/MDI and PPG 400/MDI (−28°C and 26°C) are for homopolyurethane matrices in which complete conversion of –OH and –NCO groups (to urethane) has been achieved. Introducing diacetylene-based HS in the uncured copolyurethanes, PPG 1000/HDD/MDI and PPG 400/HDD/MDI, results in small decreases in T_g (−32°C and 23°C). This occurs because in the uncured materials, conversion of –OH groups on PPG to yield higher molar mass poly(ether–urethane) SS is incomplete, as is the reaction via urethane formation with the developing poly(diacetylene–urethane) HS. Nevertheless, despite incomplete reaction, a significant amount of conversion has occurred since the T_g of totally unreacted PPG is ~−65°C. Also in the uncured materials, the degree of phase separation is high as indicated by the values of PSR (>85%). The high degree of phase separation is surprising since the uncured materials were formed at 80°C (increasing to ~120°C with the exotherm) which is around T_g of the HDD/MDI HS. Under these conditions, HS vitrification is delayed and phase separation is reduced. However, the development of HS molar mass (which must be sufficiently high in the first place for vitrification and phase separation to occur) may be affected by the small amount of cross-polymerization occurring, which reduces molecular mobility and the ability of HS oligomers to further react. Cross-polymerization may also lead to the formation of HS domains with sizes smaller than would otherwise be the case in solely linear systems.

In the cured materials, PPG 1000/HDD/MDI and PPG 400/HDD/MDI, –OH and –NCO reactions are complete. All PPG chains are connected via urethane groups into the SS matrix and to HS whose mean length has been increased. In addition, cross-polymerization has been maximized (but not completed). During cure (120°C/36 h) which is well above HS T_g (85°C), full PU development and the increased crosslinking in the HS phase have caused extensive phase mixing to occur as shown by the significant reduction (~20%) in PSR values. Consequently, T_g values for the cured copolyurethanes, PPG 1000/HDD/MDI and PPG 400/HDD/MDI, have increased by 19 and 14°C, respectively, to values well above those for PPG 1000/MDI and PPG 400/MDI (the isolated SS matrices). Larger effects are observed for the PPG 1000-based system, since the longer polyether chains, lower HS content and degree of cross-polymerization allow greater molecular mobility and easier phase mixing in the copolyurethane.

Values of T_{cp} in *Table 2* show that the maximum rate

Table 2 Thermal transitions (d.s.c.) of homopolyurethanes and urethane–diacetylene copolymers

Material	HS (%)	$T_g{}^a$ (°C)	$T_g{}^b$ (°C)	$T_{cp}{}^a$ (°C)	$T_{cp}{}^b$ (°C)	PSR[a](%)	PSR[b](%)
PPG1000/MDI	0	–	−28	–	–	–	–
PPG1000/HDD/MDI	22.4	−32	−13	245	248	86	65
PPG400/MDI	0	–	26	–	–	–	–
PPG400/HDD/MDI	33.5	23	37	235	235	89	70
HDD/MDI	100	ND	85[c]	230	230	–	–

[a] Uncured (partially reacted, lightly cross-polymerized)
[b] Cured 120°/36 h (completely reacted, highly cross-polymerized)
[c] Quench-cooled sample (280 to −100°C)
Not detected = ND

of topochemical cross-polymerization in HS domains, occurring between 230°C and 250°C, is not affected by the materials thermal history (during formation or curing). The intensity of the exotherm however, which is proportional to the concentration of diacetylene units in HS domains, is significantly reduced by a factor of three in both copolymers. Thus, given the higher HS content and phase separation in PPG 400/HDD/MDI, it would appear that the efficiency and degree of cross-polymerization achieved in these materials are greater for copolyurethanes based on higher molar mass SS; that is, PPG 1000 compared with PPG 400.

Dynamic mechanical thermal behaviour

Modulus–temperature and mechanical damping–temperature behaviour were obtained over the temperature range -150 to 200°C using the d.m.t.a. technique described earlier. Typical $\log(E')$ and $\tan\delta$ *versus* temperature plots for the homo- and copolyurethanes based on PPG 1000 and PPG 400 are shown in *Figure 6*. Considering first the damping curves, the linear homopolyurethanes, PPG 1000/MDI and PPG 400/MDI, both show three relaxations which, in order of decreasing temperature are designated α, β and γ. The α-transition is clearly the most intense and is associated with the glass transition of the polymer, located at T_g. The lower intensity peaks, β and γ, are secondary relaxations attributed to molecular motions associated with water–urethane complexes and oxypropylene units in polyether-rich domains, respectively. The temperatures and peak intensities of α-, β- and γ-relaxations are summarized in *Table 3*. The modulus–temperature behaviour for these two homopolyurethanes is similar with the significant reduction in $\log(E')$ occurring at T_g followed by a small rubbery region before decreasing rapidly (coinciding with the sharp rise in $\tan\delta$) as the materials transform to the liquid state. The main differences between PPG 1000/MDI and PPG 400/MDI occur with the location of T_g and the value of rubbery modulus above T_g, both of which are increased as the molar mass of the PPG used in PU formation is decreased (or the relative proportion of aromatic MDI to aliphatic polyether is increased).

Incorporating cross-polymerized, urethane–diacetylene HS into both materials results in significant increases in $\log(E')$ and reductions in $\tan\delta$ as functions of temperature, as seen in *Figure 6c* and *d* for PPG 1000/HDD/MDI and PPG 400/HDD/MDI. Most notable is the 25–30°C rise in T_g* and the corresponding 30–40% decrease in the peak value of $\tan\delta$ (as well as the broadening of the peak). These changes are due to the phase mixing between polyether SS and poly(urethane–diacetylene) HS, as indicated previously by the values of PSR in *Table 2*. On the basis of the footnote and the

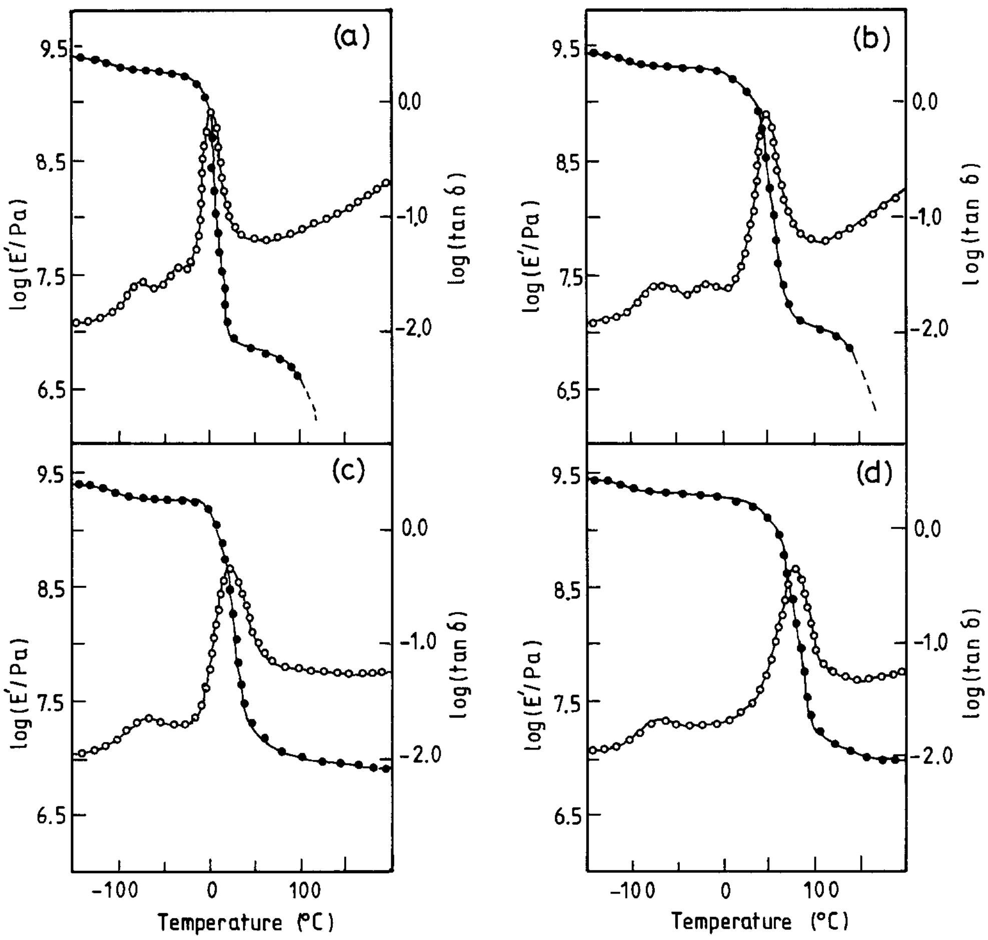


Figure 6 Dynamic mechanical-thermal analysis curves (1 Hz) of storage flexural modulus (E') and mechanical damping ($\tan\delta$) *versus* temperature for homopolyurethanes (a) PPG 1000/MDI and (b) PPG 400/MDI, and corresponding highly cross-polymerized copolyurethanes (c) PPG 1000/HDD/MDI and (d) PPG 400/HDD/MDI

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* T_g values in *Table 3* correspond to the T_g values in the second column of *Table 2* (d.s.c.). The 20–40°C differences in T_g values are attributed to differences in d.s.c. and d.m.t.a. techniques and the analysis methods used to determine T_g from experimental data

Table 3 Dynamic mechanical thermal properties of homopolyurethanes and urethane–diacetylene copolymers

Material	HS (%)	α (T_g) (°C)	tan δ (max)	β (°C)	tan δ (max)	γ (°C)	tan δ (max)
PPG1000/MDI	0	0	0.74	-30^a	0.02	-68	0.03
PPG1000/HDD/MDI	22.4	25	0.45	–	–	-65	0.02
PPG400/MDI	0	45	0.72	-15	0.02	-68	0.03
PPG400/HDD/MDI	33.5	75	0.48	–	–	-64	0.02

[a] Approximate value: shoulder merged with α (T_g) transition

value of T_g (85°C by d.s.c.) reported in *Table 2* for HDD/MDI, the value of T_g by d.m.t.a. for the isolated HS would be expected to be between 110°C and 115°C. The closer proximity of T_g for PPG 400/HDD/MDI to that of HDD/MDI, compared with PPG 1000/HDD/MDI, is directly attributed to the higher HS content of the former copolymer. The damping curves for the copolymers also show that the β-peak has disappeared, which is presumably due to reduced moisture adsorption, compared with the homopolyurethanes. In addition, there is a small, but noticeable increase in temperature location of the γ-peak (from -68 to -64°C) and a corresponding reduction in the peak value of tan δ (0.03 to 0.02) for the copolymer. This again confirms that phase mixing has occurred during cross-polymerization of these materials.

The biggest effects on modulus–temperature behaviour of incorporating cross-polymerized, HS is observed above T_g by the higher values of log (E') and the extended rubbery modulus plateau (coinciding with the steady level of damping in this temperature region). The d.m.t.a. data clearly show that the otherwise linear homopolyurethanes are transformed into non-linear copolyurethanes with improved modulus– and damping–temperature behaviour. The copolymer materials are characterized by intermediate degrees of phase separation and by crosslinking which is due entirely to cross-polymerized, PU–diacetylene HS.

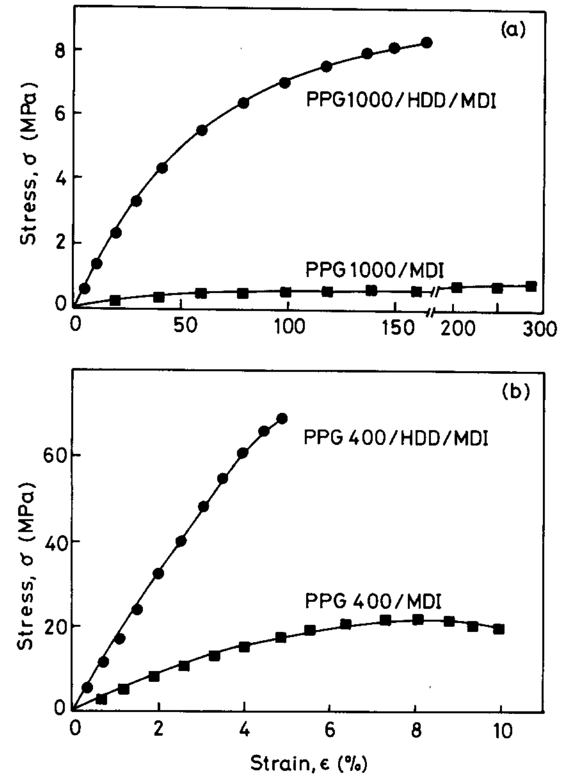

Figure 7 Tensile stress–strain curves (23°C) for homopolyurethanes and highly cross-polymerized copolyurethanes based on (a) PPG 1000 and (b) PPG 400

Tensile stress–strain properties

Tensile measurements were carried out at 23°C using dumb-bell specimens of gauge length 30 mm and an extension rate of 1 mm min^{-1}. Average stress–strain curves are shown in *Figure 7a* for PPG 1000/MDI and PPG 1000/HDD/MDI, and in *Figure 7b* for PPG 400/MDI and PPG 400/HDD/MDI. Tensile properties derived from these curves are summarized in *Table 4*.

The linear homopolyurethane, PPG 1000/MDI, has a T_g of 0°C (d.m.t.a.) and at room temperature, therefore, behaves as a very soft, weak and friable elastomer. Incorporating only 22.4 w/w% of HS increases stiffness and strength by factors of $\sim$20 and 15, respectively, whilst only halving ultimate elongation. Consequently, copolymer PPG 1000/HDD/MDI is nearly an order of magnitude tougher. This transformation in mechanical behaviour arises from both the upward shift in T_g to 25°C and the reinforcing effects resulting from the stiff, highly crosslinked poly(urethane–diacetylene) HS. In the case of PPG 400/MDI, which has a T_g of 45°C (d.m.t.a.), the material exhibits the 'leather-like' characteristics of a linear polymer in its transition region; that is, an intermediate value of modulus (10^8–10^9 Pa) and ductile deformation behaviour with slight evidence of yielding (see *Figure 7b*). Incorporating a higher level of HS (33.5 w/w%) however, produces less dramatic changes in relative terms, compared with PPG 1000/MDI. Nevertheless, the copolymer PPG 400/HDD/MDI is transformed into a strong, glassy and tougher material. The significant upward shifts in T_g to 75°C and the reinforcing effects of the cross-polymerized HS again account for these changes in tensile properties.

The two copolyurethane systems studied are essentially molecular composites. In the PPG 1000 system the cross-polymerized HS reinforce a rubbery matrix whereas in the PPG 400 system the matrix is relatively glassy and is reinforced to a lesser degree. In both cases the HS should be, to a first order approximation, identical in structure and properties and so will have the same modulus (which is unknown at this stage). Since both the unreinforced and reinforced values of modulus and the HS contents are known for both materials it should be possible to determine the effective HS modulus E_{HS} using composite analyses. Unfortunately simple Voigt or Reuss averaging procedures[22] do not yield a unique value of E_{HS} since it appears that neither a uniform strain nor a uniform stress situation is applicable. A more appropriate approach is to use the Takayanagi models

Table 4 Tensile properties of homopolyurethanes and urethane–diacetylene copolymers

Material	HS (%)	E (MPa)	σ_u (MPa)	ε_u (%)	U_t (MJ m^{-3})
PPG1000/MDI	0	0.8	0.57	280	0.001
PPG1000/HDD/MDI	22.4	15.8	8.35	165	0.009
PPG400/MDI	0	482	20.32	4.0	1.503
PPG400/HDD/MDI	33.5	1594	67.65	2.2	2.423

Abbreviations: E, Young's modulus; σ_u, ultimate tensile stress; ε_u, ultimate tensile strain; U_t, total fracture energy

which have been employed extensively by Ward and co-workers[23,24] and others[25,26] to model the elastic properties of semicrystalline polymers particularly when one phase is dispersed within the other phase. The general forms of these models are the so-called series–parallel and parallel–series cases. Although both models have been evaluated in this present study and gave similar results, only the results for the series–parallel model, shown in *Figure 8*, will be presented. In this model, the copolyurethane (composite) modulus, E, is given by

$$\frac{1}{E}=\frac{(1-\Phi)}{E_{ss}}+\left[\frac{\Phi}{\lambda E_{HS}+(1-\lambda)E_{ss}}\right] \qquad (1)$$

where E_{ss} is the SS (homopolyurethane) modulus and ϕ and λ are the volume fractions of HS parallel and perpendicular, respectively, to the applied stress. The volume fraction of HS, V_{HS}, is then given by

$$V_{HS}=\phi\lambda \qquad (2)$$

To a first approximation V_{HS} can be assumed to be the same as the weight fraction of hard segments given in *Table 4*. Equation (2) contains essentially two unknown parameters, either ϕ or λ (related through V_{HS}) and E_{HS}. Examination of the equation has shown that for the PPG 1000 system for E_{HS} to be finite then $\phi > 0.95$. It is possible for a given value of V_{HS} to vary ϕ (and λ through equation (2)) in equation (1) and generate different values of E_{HS}. This has been done in *Figure 9* for the two systems using appropriate values of E, E_{ss} and V_{HS} (from *Table 4*) in the range $0.9 < \phi < 1.0$. It can be seen that for the elastomer $E_{HS} \rightarrow \infty$ when $\phi < 0.95$ whereas for the glass E_{HS} increases steadily as ϕ decreases. A single value of E_{HS} of about 5 GPa is generated when ϕ is approximately equal to 0.95. The values of each of the parameters are listed in *Figure 9*. It is likely that the two systems have similar morphologies and the same value of ϕ for both systems would not be unreasonable.

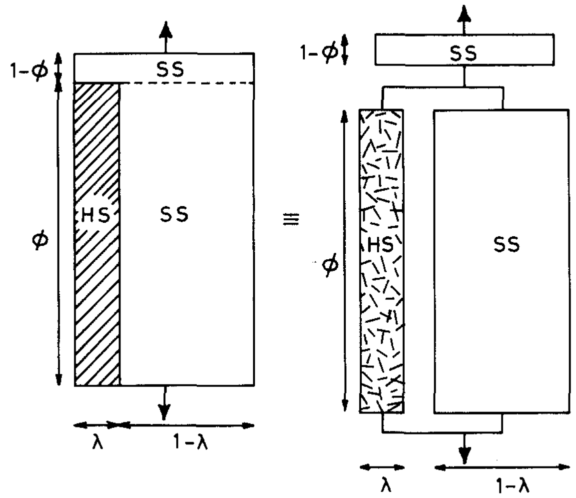

Figure 8 Generalized Takayanagi model of a urethane–diacetylene copolymer with a continuous poly(ether-urethane) soft-segment phase, SS. The model breaks down (right) into series and parallel components of volume fractions $(1-\phi)$ and ϕ, with the latter comprising fractions $(1-\lambda)$ of SS and λ of randomly oriented, poly(urethane-diacetylene) hard segments, HS

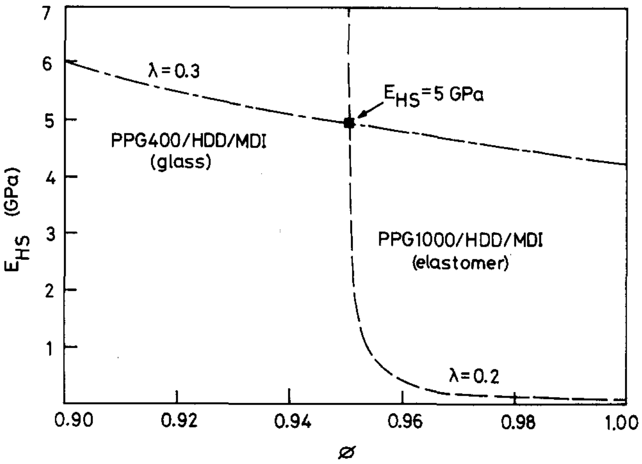

Figure 9 Variation of HS modulus, E_{HS}, with volume fraction, ϕ, of the HS/SS parallel component in the series–parallel model (*Figure 8*) used to represent the tensile deformation of urethane–diacetylene copolymers. Theoretical curves are calculated from the data of *Table 4* using equations (1) and (2)

The question that arises is that of the significance of a value of E_{HS} of 5 GPa. Although the exact structure and morphology of the HS has not been determined it is likely that they are as shown in *Figure 4* consisting of aligned polydiacetylene backbones with PU crosslinks and hydrogen bonding parallel to the polydiacetylene chain direction. It is likely that the structure shown in *Figure 4* also packs into layers parallel to the page which are held together by van der Waals bonds. This structure is not unlike that of urethane-substituted polydiacetylene single crystals[10,27]. Such polymers are known[10] to have highly anisotropic mechanical properties with the Young's modulus in the chain direction much higher than the transverse moduli both parallel and perpendicular to the hydrogen-bonded planes. Typical chain direction moduli of 50–60 GPa have been measured for polydiacetylene single crystals[10,27] whereas transverse moduli are generally of the order of 1 GPa (ref. 10). The present segmented copolyurethanes however, are isotropic since the orientation of the HS in these materials is random as shown schematically by the discontinuous lines in the HS fraction, λ, of the right-hand part of *Figure 8*. Thus, an 'average' value for the modulus of the HS fraction is obtained from the analysis outlined. The value of this average modulus will depend upon deformation due to stresses at all angles to the chain direction and a generated value of E_{HS} of 5 GPa would seem to be very reasonable. During general deformation of the materials the values of stress and strain within the HS will depend upon the exact orientation of the polydiacetylene molecules in the HS in relation to the deformation axes. Clearly, a more sophisticated technique giving greater detailed analysis is required to examine these localized stresses and strains, and their distributions between the different phases, in relation to the gross deformation of these types of copolymer materials. Such a technique is afforded by Raman spectroscopy, which has been used to investigate the micromechanics of deformation in these materials.

DEFORMATION MICROMECHANICS OF URETHANE–DIACETYLENE COPOLYMERS USING RAMAN SPECTROSCOPY

Raman spectroscopy: experimental

Raman spectra were obtained from cross-polymerized samples using a Raman microscope system. This is based upon a SPEX 1403 double monochromator connected to a modified Nikon optical microscope. Spectra were obtained at a resolution of the order of $\pm 5\,\mathrm{cm}^{-1}$ using the 632.8 nm line of a 10 mW He/Ne laser. A ×40 objective lens with a numerical aperture of 0.65 was employed and this gave a $2\,\mu\mathrm{m}$ spot when focused (although the objective lens was generally defocused to reduce the possibility of damage through excessive heating). In the case of deformed samples, the laser beam was always polarized parallel to the tensile axis.

Spectra were obtained from the surface of strips of cross-polymerized material, approximately $2 \times 10 \times 50$ mm, during deformation using a Polymer Laboratories 'Mini-mat' mechanical testing machine. This is designed specifically to fit onto the stage of an optical microscope. The strips were deformed to fixed displacements using a gauge length of the order of 30 mm. The strain was determined from the gauge length and the displacement. The load on the specimen was also monitored using a 200 N load cell. Each spectrum was determined over a period of about 10 min. It was found that stress relaxation took place during deformation over this period of time and the stresses quoted are mean values.

Analysis and discussion of Raman spectra

It was found that Raman spectroscopy could be used to obtain spectra from cross-polymerized samples of the copolymers. *Figure 10* shows a series of spectra for the HDD/MDI pure HS (*Figure 10a*), the PPG 400/HDD/MDI glass (*Figure 10b*) and the PPG 1000/HDD/MDI elastomer (*Figure 10c*). A broad fluorescent background was obtained for the HDD/MDI HS but this was found to decrease between *Figure 10a* and *c* with the incorporation of the PPG SS and as the length of the SS increased. This was probably due to both an increase in order and a reduction in the proportion of MDI aromatic groups. The spectra are similar to those obtained by Rubner[7] for his radiation-polymerized PU–diacetylene copolymers. The spectra in *Figure 10* contain Raman bands at 1450 and $2100\,\mathrm{cm}^{-1}$ which are characteristic of the double and triple bond vibrations of the conjugated backbone of the diacetylene units[8]. The variations between the Raman spectra depend upon coupling of the motion of the side group atoms with that of the backbone atoms. It can be seen that there are some slight differences in the spectra below $1400\,\mathrm{cm}^{-1}$ due probably to local variations in the flexibility of side group structures. However, the two main peaks of interest at 1450 and $2100\,\mathrm{cm}^{-1}$ are essentially identical.

One of the main aims of this study was to determine the effect of deformation upon the position of the $-\mathrm{C{\equiv}C}-$ triple bond stretching band in the glass and elastomer. It was found that for both materials subjected to an applied tensile strain, the position of the band shifted to lower frequency as can be seen in *Figure 11a* for the PPG 400/HDD/MDI glass and in *Figure 11b* for the PPG 1000/HDD/MDI elastomer. In both cases there is a significant decrease in the peak frequency of the Raman band coupled with the broadening of the band.

The effect of deformation upon the peak position is shown in more detail for the PPG 400/HDD/MDI glass in *Figure 12*. The effect of applied strain is shown in *Figure 12a* and that of applied stress in *Figure 12b*. In both cases there is a linear shift and the rates of shift are

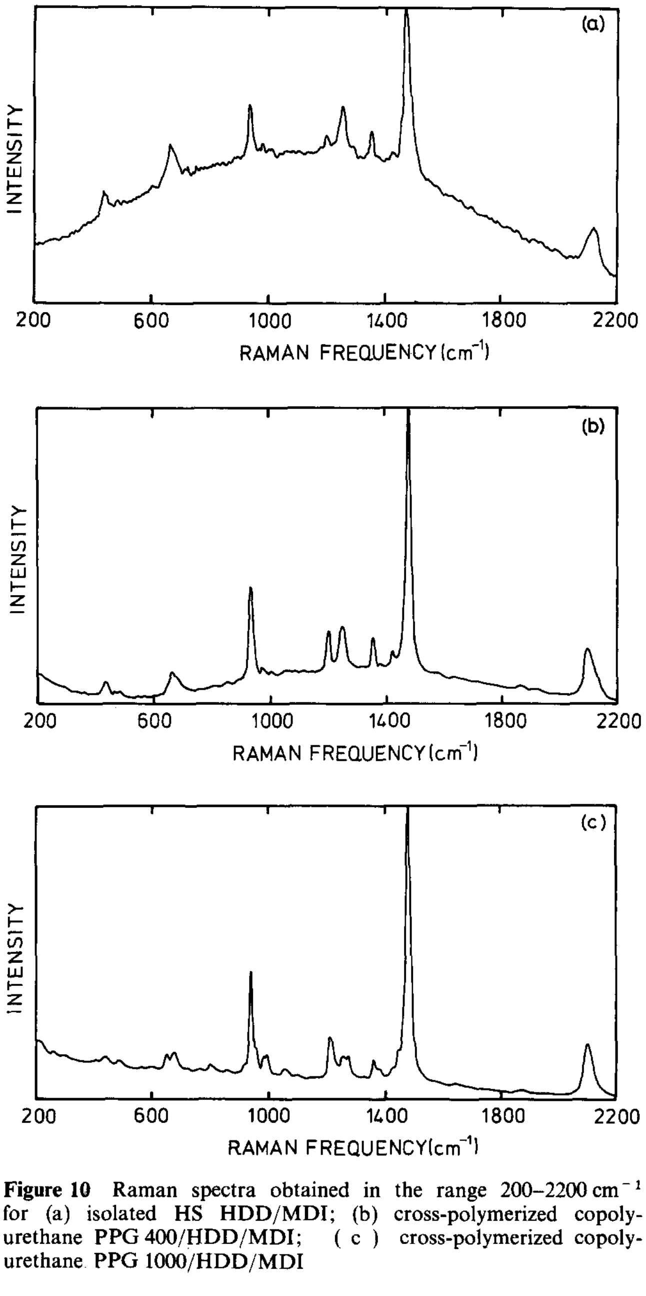

Figure 10 Raman spectra obtained in the range $200\text{–}2200\,\mathrm{cm}^{-1}$ for (a) isolated HS HDD/MDI; (b) cross-polymerized copolyurethane PPG 400/HDD/MDI; (c) cross-polymerized copolyurethane PPG 1000/HDD/MDI

listed in *Table 5*. It should be noted that the value of Young's modulus determined from the data in *Figure 12* is significantly lower than that obtained from *Figure 7b*. This is because the deformation of the material is rather strain-rate sensitive due to the proximity of the T_g (*Table 3*). The effective strain rate for *Figure 12* is several orders of magnitude less than that used in *Figure 7b*.

The effect of deformation upon the peak position for the PPG 1000/HDD/MDI elastomer is shown in *Figure 13*. In this case significantly higher strains could be applied because of the higher elongations possible for the elastomer (*Figure 7a*). It can be seen from *Figure 13a* that there is a significant decrease in the Raman frequency, $\Delta\nu$, with applied strain but that the change is not linear. On the other hand, the shift in $\Delta\nu$ with applied stress shown in *Figure 13b* is found to be linear within the bounds of experimental error. The significance of this behaviour will be discussed later.

The shifts in the Raman bands with deformation were found to be reversible and there was found to be a shift to high frequency when the stress and strain were decreased. This behaviour is shown in *Figure 14* for the PPG 1000/HDD/MDI elastomer. Another point to note from *Figure 14* is that when the elastomer is subjected to high degrees of deformation ($\varepsilon > 50\%$) multiple peaks are obtained in the Raman spectrum. It can be seen that the band for triple bond stretching in *Figure 14* shows several peaks when the material is deformed to a strain of 60%. This is indicative of significant local variations in stress and strain in the HS. It follows a gradual broadening of the Raman band with increasing deformation and could be due to break-up of the HS.

The stress- and strain-induced Raman frequency shifts in the two cross-polymerized materials give a unique insight into the micromechanics of the deformation of the HS in the materials. The analysis of substituted polydiacetylene single crystals using Raman spectroscopy[10] has shown that when such crystals are deformed parallel to the chain direction, the position of the bands for triple bond stretching shifts by about 20 cm^{-1}/% strain regardless of the crystal modulus (which is controlled by the substituent groups). Also in such materials strong Raman scattering is only obtained when the direction of the polarization of the laser beam is parallel to the axis of the polydiacetylene molecules (i.e. parallel to the fibre axis). This implies that in the materials studied the Raman scattering comes principally from polydiacetylene units in the HS which are aligned parallel to the direction of polarization of the laser beam (the stressing direction in the deformation experiments). Hence, the deformation-induced Raman frequency shifts would appear to be obtained principally from polydiacetylene units aligned parallel to the deformation axis. This means that the Raman spectroscopy essentially probes only the deformation of molecules in this particular orientation. The Raman shifts measured for the two materials are given in *Table 5*. The shifts in terms of strain are about five times higher for the glass than

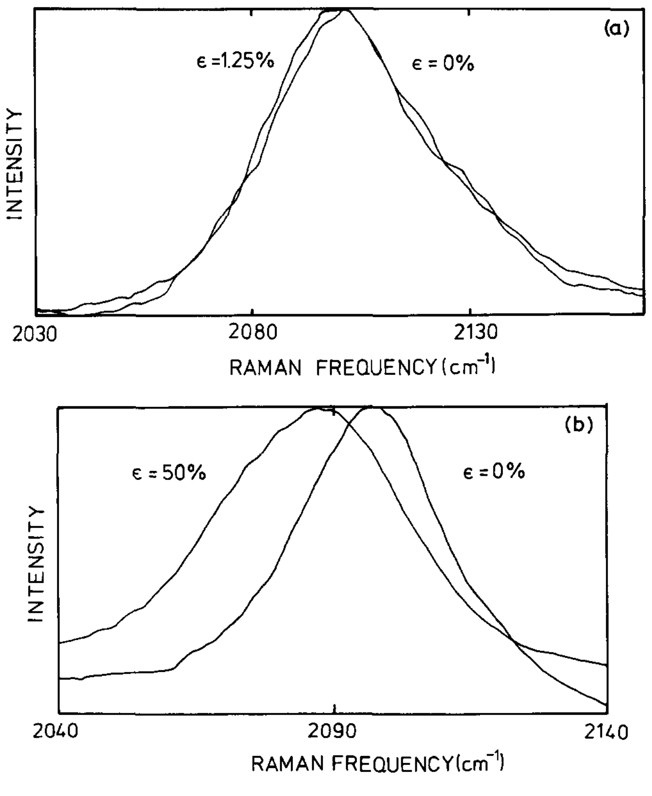

Figure 11 Raman spectra in the –C≡C– region of 2100 cm^{-1} for cross-polymerized copolyurethanes before deformation ($\varepsilon = 0\%$) and after deformation. (a) PPG 400/HDD/MDI ($\varepsilon = 1.25\%$); (b) PPG 1000/HDD/MDI ($\varepsilon = 50\%$)

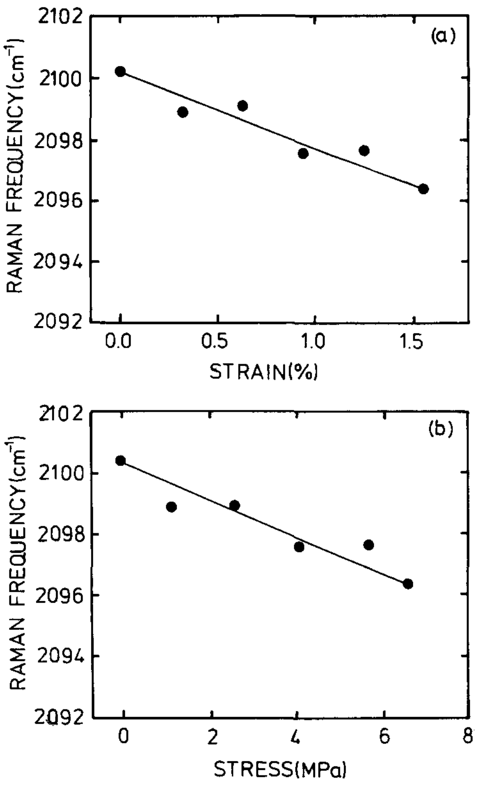

Figure 12 Variation of the position of the 2100 cm^{-1} peak in cross-polymerized PPG 400/HDD/MDI with tensile deformation. Dependence on (a) strain; (b) stress

Table 5 Effect of deformation upon the peak frequency, $\Delta\nu$, of the 2100 cm^{-1} triple bond stretching band for the cross-polymerized urethane–diacetylene copolymers

Copolymer	$d\Delta\nu/d\varepsilon$ (cm^{-1}/%)	$d\Delta\nu/d\sigma$ (cm^{-1}/MPa)
PPG400/HDD/MDI	2.5	0.54
PPG1000/HDD/MDI	0.5[a]	1.53

[a] Initial value

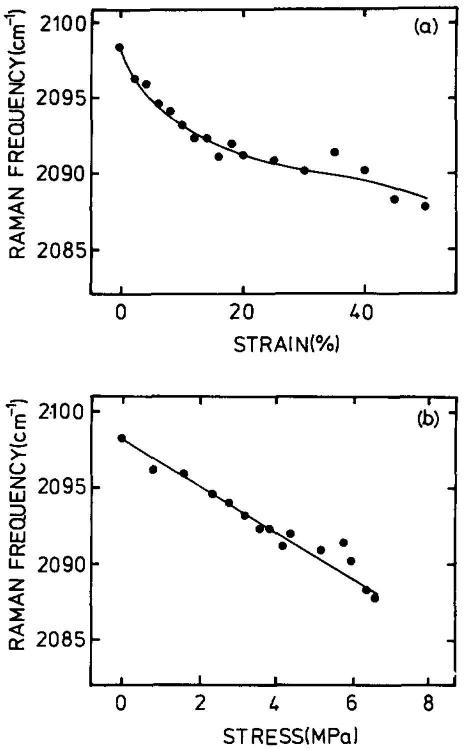

Figure 13 Variation of the position of the 2100 cm^{-1} peak in cross-polymerized PPG 1000/HD/MDI with tensile deformation. Dependence on (a) strain; (b) stress

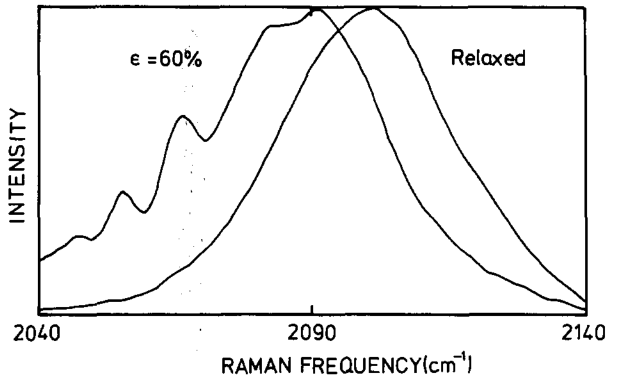

Figure 14 Raman spectra in the region of 2100 cm^{-1} for cross-polymerized PPG 1000/HDD/MDI before deformation (relaxed) and after deformation to a tensile strain, ε, of 60%, showing the development of multiple peaks

for the rubber. Analysis using the series–parallel model and determination of the local strains in the different phases have shown that at a given level of overall strain, the HS strain in the PPG 400/HDD/MDI glass is considerably higher than that for the HS in the PPG 1000/HDD/MDI rubber. This is because the modulus of the matrix in the glass is more closely matched to that of the HS than in the case of the rubber. Since the Raman measurements give a direct measure of HS strain the higher deformation-induced shift for the glass (in terms of $d\Delta\nu/d\xi$) than for the rubber is consistent with this prediction. (The reversal of this ranking when $d\Delta\nu/d\sigma$ is considered is a reflection of the higher modulus possessed by the glass.)

The series–parallel model shows that during deformation, in the case of the PPG 400 glass, the average strain in the HS is similar to the overall strain on the specimen. The rate of shift ($d\Delta\nu/d\varepsilon$) is 2.5 cm^{-1}/% strain which is much less than for a polydiacetylene single crystal which is 20 cm^{-1}/% strain[10]. However, although the average strain in the HS is similar to that of the overall specimen strain the actual strain in an individual elastically anisotropic HS will depend upon the relative orientation of its polydiacetylene chain direction with respect to the tensile axis. This anisotropy will lead to HS with their polydiacetylene chains parallel to this axis being subjected to lower strains than those in transverse direction. Since the average modulus of the HS is 5 GPa in comparison with the polydiacetylene chain modulus of 50 GPa, then the deformation-induced shifts in the glass might be expected to be a factor of 10 less than those in a polydiacetylene single crystal subjected to the same strain. This is precisely what is found since the shift for the PPG 400/HDD/MDI copolymer is 2.5 cm^{-1}/% as opposed to 20 cm^{-1}/% for a polydiacetylene single crystal.

CONCLUSIONS

This present study has shown that it is possible to prepare PU–diacetylene segmented copolymers with different physical properties using a relatively simple one-step bulk polymerization process. The earlier study of Rubner[7] had demonstrated that PU–diacetylene copolymer elastomers could be produced using solution polymerization. This work has shown that it is possible to produce glassy as well as elastomeric polymers and that bulk polymerization methods can be successfully employed. The mechanical properties of the materials have been analysed using the simple Takayanagi series–parallel model. It has been pointed out that individual HS will have anisotropic mechanical properties and the average modulus of the overall HS phase, $E_{HS} = 5$ GPa, generated by the model has been shown to be consistent with the values obtained for polydiacetylene single crystals. Rubner[7] demonstrated that the segmented copolymers have interesting and unusual optical properties. In particular he was concerned with thermochromic effects. It has been found from this present study that the positions of the bands in the Raman spectra are dependent upon stress and strain and this effect has important implications such as giving rise to the possibility of measuring strain by optical methods.

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REFERENCES

1 Van Bogart, J. W. C., Lilaonitkul, A. and Cooper, S. L. *Adv. Chem. Ser.* 1979, **176**, 3
2 Seymour, R. W., Estes, G. M. and Cooper, S. L. *Macromolecules* 1970, **3**, 579
3 Seymour, R. W., Allegrezza, A. E. and Cooper, S. L. *Macromolecules* 1973, **6**, 896
4 Seymour, R. W. and Cooper, S. L. *Rubber Chem. Technol.* 1974, **47**, 19
5 Rubner, M. F. *Polym. Mater. Sci. Eng.* 1985, **53**, 683

6 Liang, R. C. and Reiser, A. *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.* 1985, **26** (2), 327

7 Rubner, M. F. *Macromolecules* 1986, **19**, 2114

8 Batchelder, D. N. and Bloor, D. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 569

9 Galiotis, C., Young, R. J. and Batchelder, D. N. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 2483

10 Young, R. J. in 'Development in Oriented Polymers—2' (Ed. I. M. Ward), Applied Science, London, Ch. 1, 1987

11 Day, R. J., Robinson, I. M., Zakikhani, M. and Young, R. J. *Polymer* 1987, **28**, 1833

12 Robinson, I. M., Zakikhani, M., Day, R. J. and Young, R. J. *J. Mater. Sci. Lett.* 1987, **6**, 1212

13 Day, R. J., Piddock, V., Taylor, R., Young, R. J. and Zakikhani, M. *J. Mater. Sci.* 1989, **24**, 2898

14 Young, R. J. and Day, R. J. *Br. Polym. J.* 1989, **21**, 17

15 Young, R. J., Day, R. J., Zakikhani, M. and Robinson, I. M. *Comp. Sci. Tech.* 1989, **34**, 243

16 Sorenson, W. R. and Campbell, T. W. 'Preparative Methods of Polymer Chemistry', Interscience, New York, 1961

17 Hay, A. S. *Org. Chem.* 1962, **27**, 3320

18 Barksby, N., Dunn, D., Kaye, A., Stanford, J. L. and Stepto, R. F. T. in 'Reaction Injection Moulding' (Ed. J. E. Kresta), *ACS Symp. Ser.* 270, 1985, 83

19 Cawse, J. L. and Stanford, J. L. *Polymer* 1987, **28**, 356

20 Wegner, G. *Pure Appl. Chem.* 1977, **49**, 443

21 Camberlin, Y. and Pascault, J. P. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 415

22 Kambour, R. P. and Robertson, R. E. in 'Polymer Science' (Ed. A. D. Jenkins), North-Holland, London, 1972

23 Ward, I. M. 'Mechanical Properties of Polymers', 2nd Edn., John Wiley & Sons, Chichester, 1983

24 Lewis, E. L. V. and Ward, I. M. *J. Macromol. Sci.* 1980, **B18**, 1

25 Takayanagi, M., Imada, K. and Kajiyama, T. *J. Polym. Sci. C* 1966, **15**, 263

26 Tashiro, K., Wu, G. and Kobayashi, M. *Polymer* 1988, **29**, 1768

27 Galiotis, C. and Young, R. J. *Polymer* 1983, **24**, 1023