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The opto-mechanical behaviour of diacetylene-containing segmented block copolymers

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Summary

The effects of mechanical deformation on the optical properties of segmented copolyurethanes have been studied using resonance Raman spectroscopy. Linear elastomeric and glassy copolyurethanes, each containing diacetylene-urethane (DA-U) hard segment domains dispersed in a continuous polyether-urethane (PE-U) matrix, were prepared in bulk and thermally cross-polymerised in the solid state. The crosslinked copolymers produced intense Raman spectra in which the C≡C triple bond stretching Raman band at ~ 2080 cm^{-1} is well defined and shifts to lower frequency under the application of tensile stress. Shifts in Raman spectra have been used to monitor stress concentrations around defects such as holes and notches machined into copolyurethane sheets. The copolyurethanes are readily applied as surface coatings to various subtrates, and their use as optically stress/strain-sensitive materials (optical strain sensors) is demonstrated.

Introduction

Diacetylene-containing copolymers have been shown [1-3] to possess optical properties similar to polydiacetylene single crystals. In particular, such copolymers produce well-defined resonance Raman spectra associated specifically with phase-separated hard segment domains which comprise fully-conjugated polydiacetylene chains formed by *in situ* solid-state topochemical polymerisation [1].

In the case of polydiacetylene single crystals, the stress-strain dependence of band positions associated with specific back-bone stretching modes in Raman spectra has been extensively studied [4,5]. When polydiacetylenes are subjected to gross tensile stress-strain, the positions of certain Raman bands shift substantially to lower frequencies due to the macroscopic deformation being translated into direct stressing of the bonds in the polydiacetylene chains. The C≡C triple bond stretching band at ~ 2080 cm^{-1} is particularly well defined and shifts by as much as - 20 cm^{-1} per 1 % tensile strain. Analysis of this opto-mechanical phenomenon therefore enables detailed studies of the deformation micromechanics of materials to be made at the molecular level, and has been used successfully with other highly-oriented polymers and composites [6].

This paper presents the results of systematic studies carried out on a wide range of diacetylene-containing copolyurethanes, and details the effects of copolymer composition on morphological structure and thermal, mechanical and optical properties. The use of Raman spectroscopy to study the deformation micromechanics of the copolyurethanes in the form of bulk sheets and to map the distributions of stress and strain around defects such as holes and cracks machined into the sheets is presented. The optical behaviour of these copolyurethanes, when coated on to plastic, inorganic glass and metal substrates, is also presented to demonstrate their use as stress/strain-sensitive surface coatings.

Experimental

Reactants and One-Stage Bulk Processing

Linear segmented copolyurethanes were formed from 4,4'-methylenediphenylene diisocyanate (MDI), 2,4-hexadiyne-1,6-diol (HDD), and a polypropylene glycol (PPG400).

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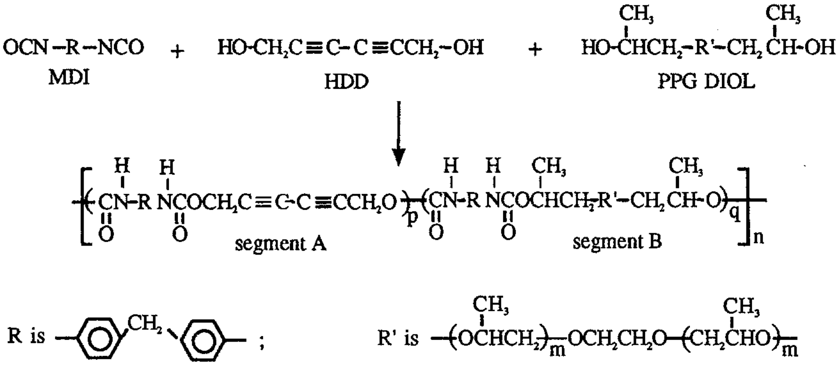
4,4'-methylenediphenylene diisocyanate, MDI, (ex.BDH), was hot-filtered (45 °C) through a 3A sinter. The equivalent weight (molecular weight per functional group as determined by end-group analysis) of the purified MDI was 125.1 g mol^{-1}.

2,4-hexadiyne-1,6-diol, HDD, was synthesised from propargyl alcohol according to the procedure reported by Hay [7]. Prior to use, HDD was recrystallised from ethyl acetate and vacuum dried for 5 hours. The purified HDD had a m.p. 112 °C (lit. 109-113 °C), and an equivalent weight of 55.0 g mol^{-1}.

Polypropylene glycol, PPG400, (ex.Fluka), was dried by rotary-film evaporation at 80 °C and had an equivalent weight of 216.6 g mol^{-1}.



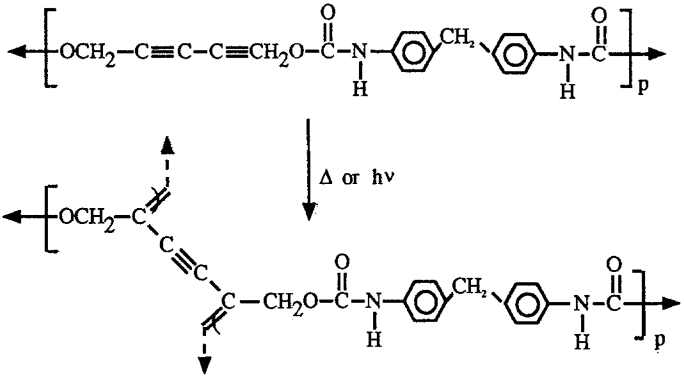
Scheme I. Linear copolyurethanes with DA-U hard segments (A) and PE-U segments (B).

Five copolyurethanes were prepared (see Table 1). The DA-U hard segment content (defined as the mass of HDD plus the stoichiometric equivalent amount of MDI, divided by the total mass of the formulation) was varied by using different proportions of HDD and PPG400. Copolymer P3a was prepared using an additional short-chain diol, dipropylene glycol, DPG, (vacuum-distilled, equivalent weight 67.0 g mol^{-1}) at approximately constant hard segment content, and the percentage weight fraction of DPG-MDI is given in parentheses in the second column of Table 1. Copolymer P4 was prepared using PPG1000 with an equivalent weight of 498.0 g mol^{-1}. All reactions were carried out using stoichiometric equivalent amounts of isocyanate and total hydroxyl groups. The copolyurethanes were produced initially as linear segmented copolymers (see Scheme I) in the form of ~3 mm thick, hand-cast sheets using a one-stage, bulk polymerisation process. The preparative details are reported elsewhere [8]. The as-prepared copolymers (except P6) were off-white, transparent/translucent materials and were readily soluble in tetrahydrofuran, and characterisation by GPC gave molar masses (M_n) in the range 8,600 to 12,040 g mol^{-1} and polydispersities between 2.0 and 2.4.

Thermal and Mechanical Properties

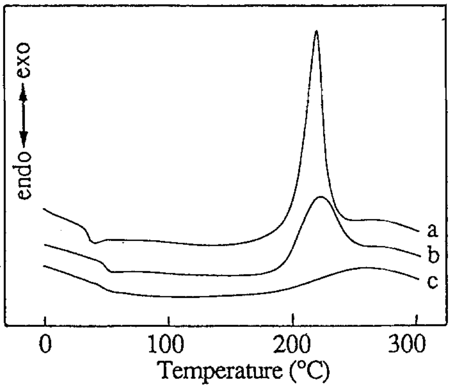
The linear copolyurethanes comprise an essentially two-phase morphology comprising rigid, highly hydrogen-bonded hard segment domains (with a distribution of sizes) dispersed in a ductile, polyether-urethane phase. The overall degree of phase separation depends on the intrinsic thermodynamic incompatibility of the chemically-distinct segments, the mutual contamination of the phases by alternative segments and on the nature of the interphase regions. The linear phase-separated copolymers are rapidly crosslinked *in situ*, using heat or radiation, either of which causes cross-polymerisation of diacetylene units within the hard segment domains. The basic chemical reaction of the diacetylene unit is shown simplistically in Scheme II in terms of a single, fully-extended DA-U chain. In practice, however, solid-state topochemical reaction involves many such chains packed within the hard segment domains, and the resulting cross-polymerisation occurs three-dimensionally. The formation of fully-conjugated polydiacetylene (PDA) chains within the phase separated copolyurethanes produces dramatic colour changes (white -> red -> deep-purple) and transforms the copolymers into completely insoluble and infusible materials. The extent of cross-polymerisation achievable in these copolymers depends on many interrelated factors, the most important being the concentration of hard segment domains and the packing efficiency or order of the DA-U chains within the domains. These factors are strongly influenced by the degree of phase separation in relation to copolymer composition (hard segment content).

The copolyurethanes were thermally treated using carefully optimised conditions of temperature and time to effect efficient cross-polymerisation and to minimise disruption and degradation of the DA-U phase. The conditions of thermal treatment were established using differential scanning calorimetry (DSC) and dynamic mechanical-thermal analysis (DMTA), and the experimental details are reported elsewhere [8]. Typical DSC curves are shown in figure 1 in which two transitions are apparent. The lower-temperature, endothermic transition at T_g (-29 °C) is associated with the main glass transition of the continuous phase, and the much more intense exothermic peak at T_{cp} (218 °C) is due to the cross-polymerisation reaction of DA-U units in hard segment domains. No endothermic behaviour associated with melting or disordering of the DA-U hard segment domains was observed, despite their apparent crystalline structure. This is probably due to the low hard segment contents and the paracrystalline nature of the domains, which provide relatively small energy changes that would be masked completely by the much more intense and extensive exothermic transition. Thermal treatment at 100 °C increases T_g to 42 °C and T_{cp} to 225°C, with a significant reduction in intensity of the exothermic peak. However, after thermal treatment at 160 °C, the glass transition is reduced and broadened, and the exothermic peak has virtually disappeared, indicating that some degradation has occurred. Increasing thermal treatment time from 20 to 40 hours at 100 °C resulted in only a small increase in the degree of cross-polymerisation (without additional degradation), and times >40 hours had little further effect.



Scheme II. Formation of a fully-conjugated polydiacetylene unit within a DA-U hard segment.

The effects of thermal treatment on dynamic behaviour are shown in figure 2 for copolyurethane P3. The damping curve (tanδ vs. temperature) for as-prepared P3 (curve a) shows three distinct peaks at increasing temperatures designated T_s, T_g and T_d. The peak at T_s (~-60 °C) is due to local relaxations involving oxypropylene units in the polyether phase. The most intense peak is ascribed to the main glass transition at T_g (50 °C), accompanied by a pronounced decrease in logE' (10^9 to 10^7 Pa) which is consistent with relaxations in the short PPG400/MDI repeat units of the chains forming the polyether-urethane phase, the major proportion of the copolymer. Despite as-prepared P3 being linear, there is a psuedo-rubbery plateau between 80 and 110 °C attributable to the presence of a high concentration of hydrogen-bonded aromatic urethane groups in the PE-U phase and the more ordered DA-U hard segment domains, both of which act as macroscopic crosslinks. As the temperature rises above 100 °C during a DMTA run, hydrogen bonds begin to dissociate and the hard segments undergo an order-disorder transition[17] and as they soften, logE' decreases and tanδ increases. However, as the temperature continues to rise, the rate of cross-polymerisation in the hard



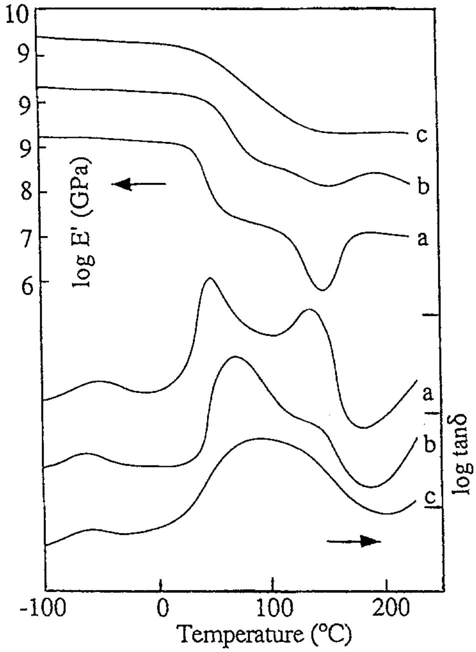


Fig.1.(above) DSC curves for copolymer P2 cross-polymerised at different temperatures.

Fig.2.(right) DMTA curves of copolymer P3 cross-polymerised at different temperatures.

(a) as-prepared; (b) 100 °C; (c) 160 °C.
[Curves displaced vertically for clarity.]

segments increases rapidly and the high degree of localised covalent crosslinking that results prevents further structural disruption. Consequently, logE' increases sharply (from 10^6 to 10^7 Pa) and tanδ decreases rapidly. The peak at T_d (~ 135 °C) arises, therefore, from the combination of two opposing molecular processes, *viz.*, reversible structural disordering and irreversible crosslinking. The final level of modulus and the minimum in tanδ are determined by the hard segment content and the efficiency of cross-polymerisation achieved within the imperfect hard segment domains, and, as the temperature exceeds 200 °C, by the onset of thermal degradation which causes logE' to decrease and tanδ to increase. Thermal treatment at 100 °C for 40 hours prior to a DMTA run, effects a substantial degree of cross-polymerisation and as curve b in figure 2 shows, the main glass transition is reduced and broadened with T_g increasing from 50 to 73 °C. Consequently, the combined peak at T_d is much less significant. Since the order-disorder transition occurs over the temperature range 110 to 140 °C, a temperature of 160 °C used during thermal treatment causes complete disruption of the hard segment domains, and efficient solid-state cross-polymerisation cannot therefore be achieved. Instead, significant phase mixing occurs and cross-polymerisation then involves only randomly-associated diacetylene units of essentially individually dispersed hard segments to produce a

Table 1. Thermal transitional behaviour (DSC and DMTA) and tensile stress-strain properties of copolyurethanes cross-polymerised at 100 °C for 40 hours.

		DSC		DMTA			TENSILE PROPERTIES		
Sample	HS (%)	T_g (°C)	T_{cp} (°C)	T_s (°C)	T_g (°C)	T_d (°C)	E (GPa)	σ_y (MPa)	ε_y (%)
P1	0	17	(a)	-65	25	(a)	0.05	(a)	(a)
P2	27	42	225	-65	65	150	1.54	39.9	3.5
P3	34	51	216	-65	73	145	1.66	51.2	3.0
P3a	33 (6)	55	220	-65	85	150	1.70	58.7	3.4
P4	22	-13	248	-65	0	(a)	0.02	8.35(b)	165(b)

(a) not observed; (b) ultimate values.

more uniformly crosslinked copolymer. The resulting DMTA curve (curve c) confirms this explanation since only a very broad, low-intensity glass transition around ~ 90 °C and a uniform high-modulus rubbery plateau are observed. Conditions of 100 °C and 40 hours were therefore shown to be optimum and used to cross-polymerise the copolymers reported in the next section.

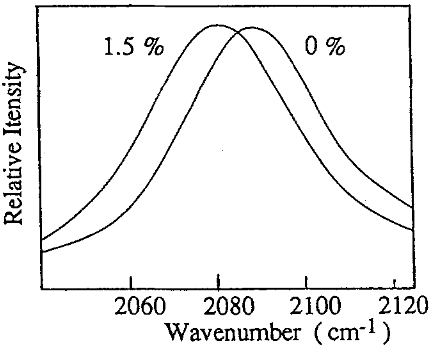
Deformation Micromechanics Studies using Raman Microscopy

Resonance Raman Spectroscopy: Experimental Procedure

The apparatus used comprised a microscope system based on a Spex 1403 double monochromator connected to a modified Nikon optical microscope. A x40 objective lens with a numerical aperture of 0.65 was used and this gave a 2 μm spot on a specimen. Raman spectra were obtained using the 632.8 nm line of a 10 mW He-Ne laser, and a charge-coupled device, CCD, camera (Wright Instruments), cooled with liquid nitrogen. The CCD camera is highly-sensitive and has very low noise, which enables Raman scattering to be detected rapidly (a scanning time of 10 s is typical for a spectral window of 40 cm^{-1}) with a resolution of 0.1 cm^{-1}. Spectra were obtained from the surfaces of cross-polymerised specimens using a small testing rig (Polymer Laboratories-Minimat) fitted onto the optical stage of the Raman microscope. Dumb-bell specimens (40 mm gauge length, ~ 3mm thick) were deformed stepwise at a rate of 1 mm min^{-1} with ~ 0.1 % tensile strain increment for each step, after which a Raman spectrum was immediately recorded over a typical exposure time of 10 s. Overall copolymer strain was measured using a resistance strain gauge attached to the dumb-bell, enabling tensile strain values to be measured to an accuracy of ± 0.0014 %.

Deformation of Copolyurethanes in Bulk, Sheet Form

The curves in Figure 3 show the position of the polydiacetylene C≡C stretching band (at 2080 cm^{-1}) for copolyurethane P3 in the undeformed and deformed states. Upon deformation, there is a pronounced shift to lower frequency and slight broadening of the Raman band. The positional shift clearly demonstrates that stress transfer from the PE-U matrix to the DA-U hard segment domains is occurring during copolymer deformation and that this stress is translated into direct deformation of the polydiacetylene chains. The dependence of C≡C band position (Δν) upon tensile strain (ε) for P3 was shown to be approximately



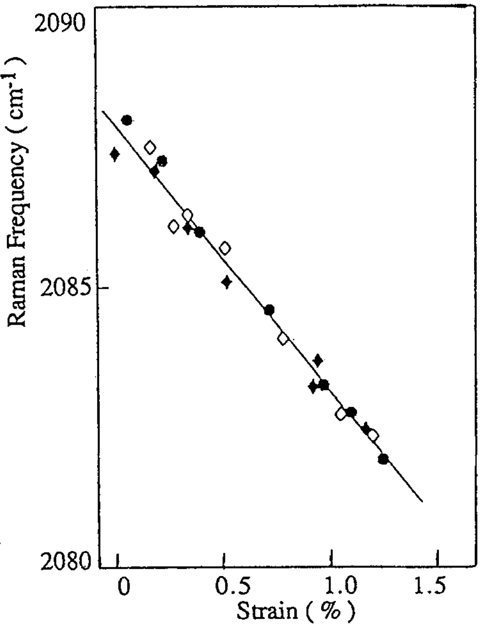


Fig.3 (above). Peak positions of the Raman C≡C band at ~ 2080 cm^{-1} for copolymer P3 at 0 % and 1.5 % tensile strain.

Fig.4 (right). Dependence of the peak position of the Raman C≡C band (~ 2080 cm^{-1}) upon tensile deformation for copolymer P3a.
-♦- loading; -●- unloading; -◊- reloading.

linear up to a value of ~ 1 % strain and as shown in Figure 4, was essentially reversible on unloading and reproducible on repeated loading. This almost linear elastic behaviour indicates that the initial deformation is borne almost entirely by the highly-crosslinked, glassy hard segment domains. As copolymer strain exceeds 1 %, yielding commences as the hard segment domains break-up and plastic deformation develops as stress is increasingly transferred to the ductile PE-U matrix. Above 1 % strain, the shift in $C\equiv C$ band position becomes increasingly non-linear with strain and decreases by over 10 cm^{-1} at copolymer strains >2 %. The overall micromechanics deformation behaviour as characterised by Raman microscopy, mirrors almost exactly the gross tensile stress-strain behaviour of the copolyurethanes and confirms that the the shifting of Raman bands is a stress-related phenomenon associated specifically with polydiacetylene chains within ordered hard segment domains.

The strain sensitivity of these copolyurethanes is determined from Raman frequency ($\Delta\nu$) versus copolymer strain (ε) plots, such as that in Figure 4, in terms of its slope, $d\Delta\nu/d\varepsilon$. The data in Table 2 show that optical strain sensitivity increases with hard segment content but is reduced on incorporating DPG. These results show clearly the dependence of Raman scattering on the presence of well-structured, polydiacetylene-containing domains, and reflect closely the structural dependence of the thermal and mechanical data described previously. Changing the nature of the copolyurethane from rigid plastic (P3) to elastomeric (P4) produces a significantly lower value of $d\Delta\nu/d\varepsilon$, due to to the much lower modulus and higher strain levels achievable for P4. The most significant results are obtained for P3 and P3a, for which the values of -6.2 and -5.3 cm^{-1} / % for $d\Delta\nu/d\varepsilon$ compare very well with -20 cm^{-1} / % reported for polydiacetylene single crystals. The lower values are explained mainly by the fact that the copolyurethanes, in contrast to the highly-anisotropic single crystals, are macroscopically isotropic and the deformation-induced Raman frequency shifts arise principally from only a minority of the polydiacetylene chains that are aligned parallel to the deformation and laser polarisation axes. Nevertheless, the data in Table 2 clearly demonstrate that these copolyurethanes can be used as optically strain-sensitive materials, and that by using Raman microscopy, strains can be measured accurately to 0.1 % with a spatial resolution of 2 µm.

Table 2. Strain sensitivity of the polydiacetylene $C\equiv C$ stretching band in segmented copolyurethanes deformed either as bulk sheets (P1 to P4) or as surface coatings (P3a-p to P3a-m).

Copolymer	HS (%)	$d\Delta\nu/d\varepsilon$ (cm^{-1} / %)
P1	0	-
P2	27	3.8 ± 1.5
P3	34	6.2 ± 0.4
P3a	33	5.3 ± 0.4
P4	22	0.5 (a)
P3a-p	33	5.5 ± 0.4
P3a-g	32	5.7 ± 0.4
P3a-m	32	5.5 ± 0.4

(a) initial value.

Deformation Distributions around Defects in Copolyurethane Plates

The use of Raman spectroscopy to determine stress concentrations around defects in copolyurethane specimens was demonstrated using 3 mm-thick plates of P3a into which circular holes and thin notches of pre-determined dimensions were machined. The specimens were deformed in tension in the Raman microscope and the change in position of the $C\equiv C$ stretching band at 2080 cm^{-1} with copolymer strain (measured remotely with a resistance strain gauge) was determined at different positions around the defects, as shown schematically by the insert in Figure 5. The slope ($d\Delta\nu/d\varepsilon$) of each line, relative to that for the remotely applied deformation data (open o) is proportional to the stress concentration at each position. For the hole, the highest stress concentration, as expected, is at the equator (solid ●) and is essentially zero at the pole (solid ♦). For the notch, stress concentration (open ◊) increases sharply depending on notch-tip radius and distance from the tip. The results obtained for the various defect geometries show the stress concentration values measured by Raman spectroscopy to be very similar to those determined from conventional stress analyses [10].

Copolyurethanes as Optical Stress-Strain Sensitive Surface Coatings

The good solublity and adhesive characteristics of the as-prepared, diacetylene-containing copolyurethanes make them attractive materials for subsequent use as surface coatings that can be applied with controlled thickness to a variety of substrates. Subsequent cross-polymerisation, *in situ* , would then convert the coatings into crosslinked materials with strain-sensitive properties that can be quantitatively determined in conjunction with the substrate, using Raman spectroscopy. To illustrate this use, ~10 % w/v solutions of copolyurethane P3a in N,N'-dimethyl acetamide (DMAc) were applied as 0.05 mm coatings to the following substrates: (a) a sheet of highly-crosslinked (non-diacetylene containing) polyurethane resin, (b) an inorganic glass filament (~25 µm diameter) and (c) a sheet of aluminium. Solvent was removed by evaporation and the coatings were thermally treated at 100 °C for 40 hours. The coated substrate specimens were deformed in tension in the Raman microscope apparatus and, as before, the shift in position, Δv, of the C≡C stretching band was monitored as a function of the overall specimen strain, ε, and in each case, excellent linearity between Δv and ε was obtained. The strain sensitivities of the three coated substrates (P3a-p, P3a-g and P3a-m), determined from the slopes of the plots, are given in the bottom three rows of Table 2, and the values of ~5.5 cm^{-1} / % for dΔv/dε are almost identical to that of the bulk sheet material, P3a. Clearly, these results demonstrate that the copolymers can be used as coatings to accurately monitor the deformation of a substrate, which is particularly useful if the substrate is of complex geometrical shape or is not readily accessible for direct measurements. As such, the polydiacetylene-containing copolyurethanes are shown to behave as optical strain gauges.

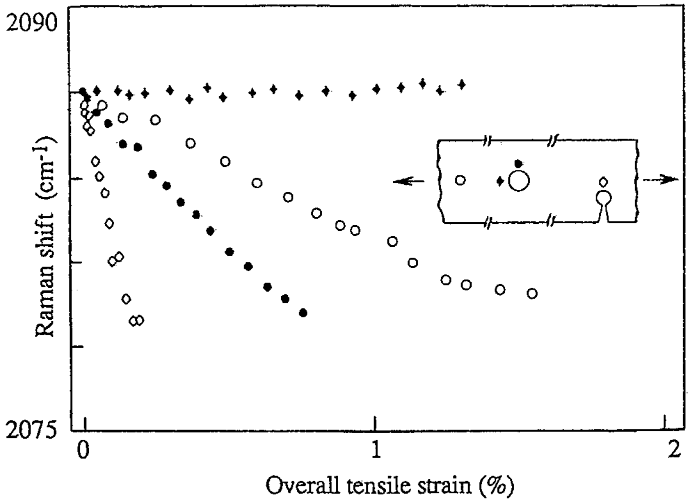


Fig.5.The effects of stress concentrations on the peak position of the Raman C≡C band (~ 2080 cm^{-1}) for a 3-mm plate deformed in tension. Data are from spectra obtained at the different indicated positions for copolymer P3a.

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