Properties of nylon-1 polymers and copolymers in the solid state

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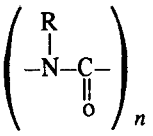
Polymers and copolymers of alkyl isocyanates have been prepared by the method of Shashoua and their properties have been investigated. All the polymers have a significant decomposition rate at 150°C but the copolymers of butyl isocyanate with ethyl isocyanate are somewhat more stable than is the butyl homopolymer. The copolymers generally show reduced crystallinity and, with high concentrations of ethyl isocyanate, substantially amorphous polymers have been prepared. Dynamic mechanical measurements give damping peaks with a fall in modulus in the temperature range of 50°–150°C but the peaks are broader and the decline in modulus less steep than for conventional vinyl polymers. Over the same temperature range the differential scanning calorimetry (d.s.c.) curves are nearly linear and show no observable discontinuity. In mechanical tests both modulus and yield stress correlate with the NCO/hydrocarbon composition ratio. The form of the stress–strain curve in tension is similar to those of cellulose derivatives. They do not show a maximum and uniform extension occurs.

INTRODUCTION

Since the polymerization of alkyl isocyanates to polymers of the 1-nylon type was first reported by Shashoua[1,2] a great deal of work has been carried out on their solution properties. It has been shown that they have a polyamide structure of the type:



$$\left(-\overset{\displaystyle R}{\overset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-\right)_n$$

and that the structure is associated with a highly extended chain conformation in solution as described by Berger[3] and Burr and Fetters[4]. For this reason a large amount of work has been carried out on the solution properties of the 1-nylons, but so far little attention has been paid to their properties in the solid state. This seemed a significant omission since it might well be expected that the physical properties of the bulk polymers would be related to their chain configuration. The only other polymers with highly linear chains which have been extensively studied to date, have been the cellulose derivatives, which, however, have a totally different chemical structure. Further, very significant differences in mechanical behaviour have been found between the cellulosics and most of the modern synthetic polymers, e.g., the former do not neck but give uniform extension under tension[5,6] whereas most synthetic polymers exhibit necking in tension after yield (unless they are brittle).

Other differences might be expected in relation to the phenomena of the glass transition (T_g). Generally, amorphous polymers in the glassy state are regarded as being frozen into one particular assembly of all the possible chain conformations. On heating above T_g all the many conformations of the molecules become accessible and interchangeable and this leads to the many well-known characteristics of the glass transition[7–9] and to the phenomena of rubber elasticity. However, if the polymer molecules have a nearly rod-like conformation, there may be no possibility of substantial changes in this conformational state above T_g and some features of the glass transition could be affected. For this reason we set out to prepare some selected nylon-1 polymers and copolymers and to study their properties in bulk.

MATERIALS AND EQUIPMENT

n-Butyl isocyanate and ethyl isocyanate were prepared from commercial materials by two fractionations through a 12 in. helix packed column in a stream of dry nitrogen. n-Hexyl isocyanate was directly synthesized by the method of Boehmer[10]. In the case of *N,N*-dimethyl formamide, the commercial solvent was distilled from calcium hydride under a stream of dry nitrogen.

Thermogravimetric analysis

A Perkin–Elmer Thermobalance TGS–1 was used with a sample weight of 1–3 mg. A heating rate of 20°C/min was adopted for all non-isothermal measurements.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) was carried out on a Perkin–Elmer DSC–2 instrument coupled to a programmable calculator with a digital readout.

^{13}C n.m.r. spectra

^{13}C n.m.r. spectra were recorded at ambient temperature on a Jeol FX–60 Fourier Spectrometer at 15 MHz in deuterochloroform.

Preparation of films

Mechanical tests were carried out on films cast on glass from toluene–chloroform (1:2 v/v) for homopolymers and

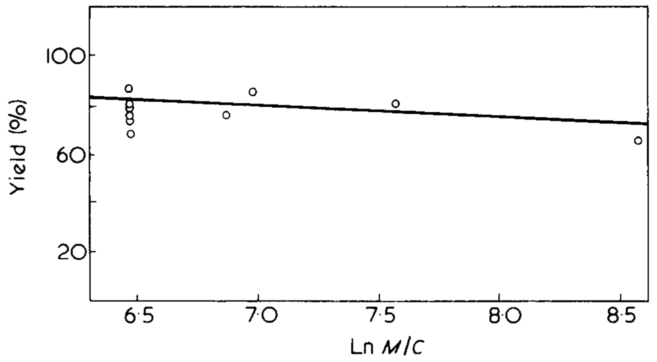


Figure 1 Effect of monomer (*M*) and catalyst (*C*) ratio on the yield of poly(n-butyl isocyanate)

chloroform–carbon tetrachloride (1:1 v/v) for copolymers. The films were dried for 26 h at 40°C and 72 h at 50°C in a vacuum oven.

Dynamic mechanical measurements

Dynamical mechanical measurements were made on cast films with a Rheovibron DDV II viscoelastometer at 11 Hz.

Tensile tests

These were carried out on an Instron Model TTM–BM at 23°C and 50% relative humidity except where otherwise stated. The test piece was to BS2782:1970 type 301K and the nominal strain rate $6.7 \times 10^{-4} s^{-1}$.

PREPARATION OF POLYMERS

Since our objective was to prepare materials for study we did not set out to make a systematic investigation of the different polymerization reactions, but a certain amount of work was necessary in order to obtain polymers of varying and controlled molecular weight in good yield. Our chosen procedure very closely followed that of Shashoua *et al.*[2] whose paper should be consulted for experimental details. All our experiments were carried out within his favourable starting temperature range of −45° to −59°C, mostly at the preferred starting temperature of −55°C.

A single experiment at −45°C with n-hexyl isocyanate confirmed Shashoua's results concerning the effect of temperature, i.e., the yield and polymer viscosity were lower than at −55°C. After addition of the catalyst (NaCN) to the monomer and solvent (*N,N*-dimethylformamide–DMF) mixture there was a rapid reaction with a rise in temperature of up to 30°C. Good yields were nearly always obtained, in the range 55–85%, but we generally obtained intrinsic viscosities above those reported previously[2] and these were also somewhat less sensitive to catalyst concentration than previously reported (*Figures 1* and *2*). However, with both butyl and hexyl isocyanate there was a rather large variability in our viscosities and the molecular weights derived from them (*Figure 2*) which however had the effect of giving us polymers with a range of molecular weights for subsequent study. Generally, however, comparison of our results with those of Shashoua, Sweeny and Tietz[2] suggests that our starting materials were probably somewhat purer than those used by Shashoua. Viscosity-average molecular weight for poly(n-butyl isocyanate) were calculated from measurements in benzene from the relation $[\eta] = 1.1 \times 10^{-5} M$ by sedimentation[11]. For poly(n-hexyl isocyanate) measurements were made in chloroform and we used the equation $[\eta] = 3.74 \times 10^{-5} M^{0.99}$ given by Berger and Tidswell[12]. In this case our molecular weights were in the range 60–240 000.

The actual values of the limiting viscosity number $[\eta]$ were generally rather high, in the range 3–15 dl/g.

PREPARATION OF COPOLYMERS

The preparation of copolymers of alkyl and aryl isocyanates is already well known as also are their copolymers with various carbonyl compounds[4,13–16]. Since our object in preparing these copolymers was to study properties in the solid state, we wished to have materials which would be reasonably rigid over the most convenient temperature range, i.e., room temperature and above. For this purpose preliminary work showed that side chains shorter than n-butyl would be preferred and for this reason we selected ethyl isocyanate as the comonomer for particular study. This monomer polymerized readily on its own but the homopolymer was insoluble in all the solvents tried and it was not further investigated.

The introduction of ethyl isocyanate appeared to make very little difference to the polymerization reaction. An apparent upward trend of yield with monomer/catalyst ratio (*M/C*) was observed, at different comonomer concentrations but in view of the scatter of results we did not consider that there were significant differences observed from those for butyl isocyanate alone. There was also some evidence that intrinsic viscosities increased with *M/C* but above 50% ethyl isocyanate it was necessary to change from benzene to chloroform as the solvent for viscosity measurement. Thus the copolymer viscosities give only a qualitative indication that the materials were of high molecular weight.

However there was good evidence that copolymers were obtained. Elemental analysis showed a direct relation between monomer feed and polymer composition in the conversion range of 60–90% (*Figure 3*) and the polymers obtained were all completely soluble in benzene or chloroform, while poly(ethyl isocyanate) was not. An indication of the changes in solubility with composition is given in *Table 1*. I.r. spectra also showed that the copolymers contained bands characteristic of each homopolymer as well as a small absorption at 1245 cm^{-1} not present in either homopolymer.

Similarly, ^{13}C n.m.r. studies of the copolymer in $CDCl_3$ solutions of the copolymer showed, in addition to the $N\text{-}\underline{C}O\text{-}N$ resonance to low field, six distinct resonances. Four of these closely match the resonances of a similar solution of homopoly(n-butyl isocyanate) and the remaining two are plausibly assigned to the methyl and CH_2 resonances from ethyl isocyanate copolymerized in the polymer. (^{13}C solution studies on poly(ethyl isocyanate) are, of course, ruled out by its insolubility in the usual solvents.)

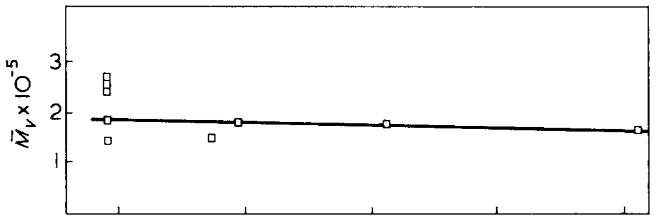


Figure 2 Effect of monomer catalyst ratio on molecular weight of poly(n-butyl isocyanate)

We concluded from these data that a true copolymer had been made.

ESTIMATES OF CRYSTALLINITY

X-ray diffraction patterns were determined on homopolymers and copolymers using the same cast films as were used in mechanical tests. A Picker powder diffractometer using CuKα radiation provided plots of scattered intensities against Bragg angle (2θ) for values of 4° to 40° as shown in *Figure 4*. The measurements were standardized with α-quartz.

The crystalline and amorphous contents were measured directly from the total area under the crystalline bands (with $2\theta_{max}$ value of 4.5°, 6° and 10°) and the broader amorphous band ($2\theta_{max}$ at 11°). The analysis was limited by the method of curve fitting, but relative crystallinities were estimated reproducibly within 5–10%.

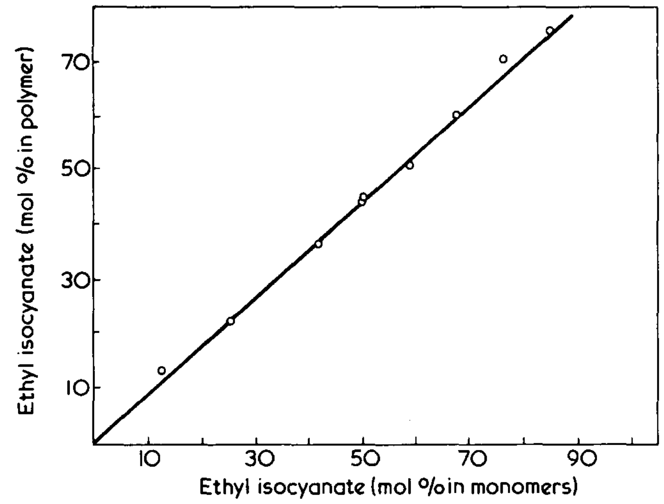


Figure 3 **Relationship between feed and polymer composition in the copolymerization of ethyl and butyl isocyanates**

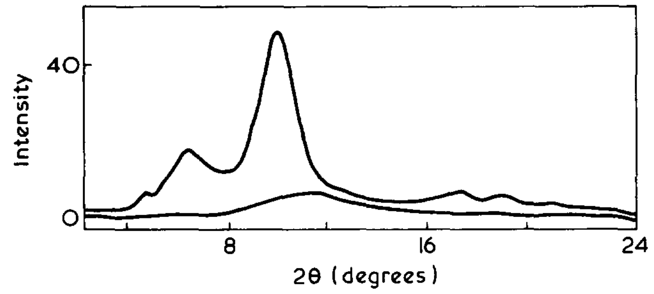


Figure 4 **X-ray diffraction patterns for poly(n-butyl isocyanate) and for a 40% ethyl isocyanate copolymer (lower curve)**

Despite the limited accuracy of the procedure it was fully adequate to demonstrate that the crystallinity of the n-butyl isocyanate polymer could be greatly reduced by copolymerization with suitable quantities of ethyl or propyl isocyanates as shown in *Figure 5*.

THERMAL ANALYSIS

Thermal stability

The thermal stability of polymers and copolymers may be conveniently measured by thermogravimetry. Generally this may be done in two ways, either the weight loss may be measured at one temperature as a function of time *or* the temperature may be raised steadily and the weight loss plotted against temperature. We found that the first method gave the most satisfactory results and in *Figure 6* we present a typical set of curves for 2 butyl isocyanate polymers of different molecular weights and for a series of copolymers. The improvement in thermal stability with increasing molecular weight was particularly well illustrated by the hexyl isocyanate polymers[23] so that molecular weight as well as composition must be assumed to affect the rate of formation of volatile products. Nevertheless it is clear that the copolymers are more stable than the homopolymers although this increase in stability is still quite limited.

Differential scanning calorimetry (d.s.c.)

These measurements were aimed at obtaining information on the behaviour of the semicrystalline and amorphous

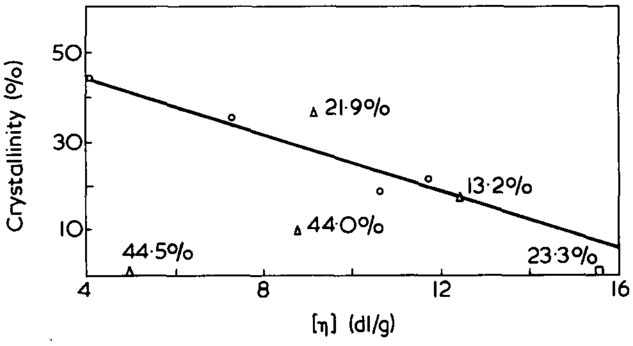


Figure 5 **Effect of copolymer composition on the estimated crystallinity of cast films of butyl isocyanate polymers and copolymers. ○, Poly(butyl isocyanate); △, butyl isocyanate–ethyl isocyanate copolymer; □, butyl isocyanate–n-propyl isocyanate copolymer. Numbers indicate percentage of comonomer**

Table 1 Solubility properties of the copolymer

Polymer	THF	Benzene	Toluene	Carbon tetrachloride	Chloroform	1,2,4-Trichlorobenzene–chloroform (75/25 v/v)
n-Butyl isocyanate	S	S	S	S	S	S
Ethyl isocyanate	Ins	Ins	Ins	Ins	Ins	Ins
BuNCO-co-EtNCO						
(13.4)–(50)	S	S	S	S	S	ND
(59)–(76)	Ins	SS	Ins	S	S	ND
(85)	Ins	Ins	Ins	Ins	Ins	SS

Numbers in parenthesis indicate range of ethyl isocyanate (mol %) in monomer (feed)
S = soluble; SS = slightly soluble; Ins = insoluble; ND = not determined

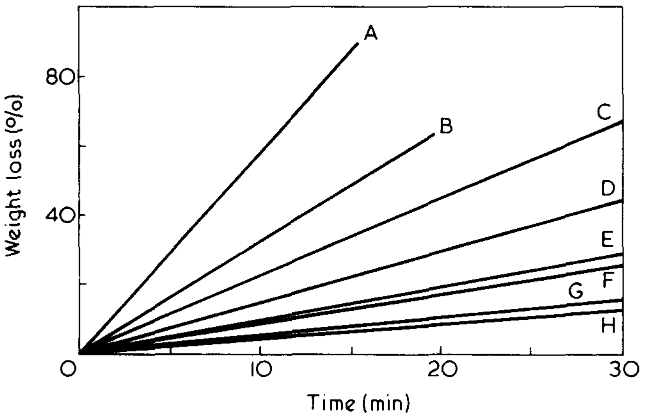


Figure 6 Weight loss for polymers and copolymers heated at 150°C.

Curve	Sample	[η] (in benzene)
A	Poly(n-butyl isocyanate)	4.2
B	Poly(n-butyl isocyanate)	7.3
C	50% Ethyl copolymer	4.9
D	13% Propyl copolymer	15.6
E	26% Ethyl copolymer	9.2
F	50% Ethyl copolymer	8.8
G	13% Ethyl copolymer	12.5
H	68% Ethyl copolymer	5.4 (in chloroform)

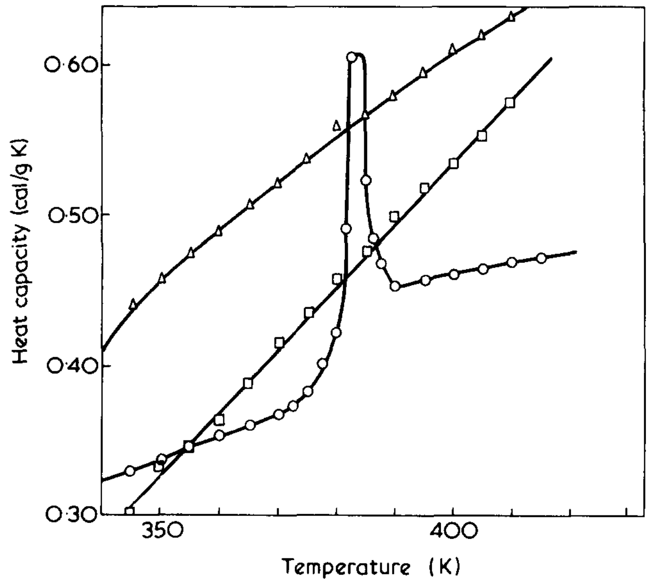


Figure 7 Differential scanning calorimetry measurements with experimental polyisocyanates compared with polystyrene. △, Poly(butyl isocyanate), [η] = 7.3; □, 44% ethyl isocyanate copolymer, [η] = 4.9; ○, anionic polystyrene

polymers over the temperature range at which softening occurs as shown by dynamic mechanical studies (see *Figures 8a* and *8b*, discussed later). It was not possible to study crystallization or melting in the d.s.c. as the polymers decomposed before melting took place.

The d.s.c. results for poly(n-butyl isocyanate) and for the ethyl isocyanate copolymer are presented in *Figure 7* over the temperature range where the modulus falls most steeply below 10^9 MN/m^2. The glass transition would be expected to lie in this range for the partly crystalline poly(n-butyl isocyanate) and must do so for the amorphous copolymer. They are compared with results obtained for polystyrene, which show in this case an endotherm as well as a clear discontinuity in C_p (ΔC_p) at the glass transition temperature. Although the actual value of ΔC_p obtained for polystyrene (measured at 10°C/min) was at 0.054 cal/g K somewhat lower than other, possibly more accurate, values of 0.064–0.077 cal/g K reported in the literature$^{17-19}$, the effect observed was highly significant. On the other hand the two polyisocyanates showed no discontinuity on C_p within the significance of the technique (±0.004 cal/g K). Thus ΔC_p, if present, must be very small and the d.s.c. method cannot be used to measure T_g with these polymers. These results confirm previous work^{20} with the simple DSC–2 which also extended down to a slightly lower temperature (40°C).

MECHANICAL PROPERTIES OF POLYMERS AND COPOLYMERS

These properties were studied in two ways: (1) as dynamic measurements using small strains in tension with a Rheovibron Viscoelastometer; (2) by conventional stress–strain curves with strains up to 50%.

Dynamic mechanical properties

The equipment used measures the Young's modulus and the loss factor (tan δ) over a wide temperature range. The results obtained are shown in *Figures 8a* and *8b* for butyl

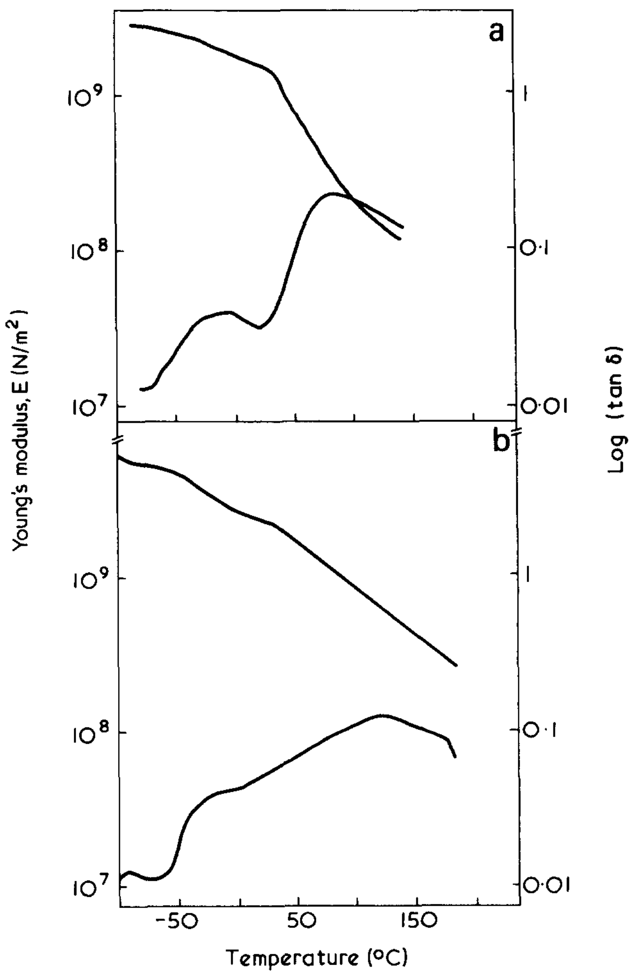


Figure 8 Modulus and damping measurements on butyl isocyanate polymers and copolymers. (a) Poly(n-butyl isocyanate), [η] = 7.3, M_w = 175000 (as in previous curves), 30–40% crystalline. (b) Butyl 44% ethyl isocyanate copolymer [η = 4.9] amorphous. Curves A, modulus; curves B, tan δ

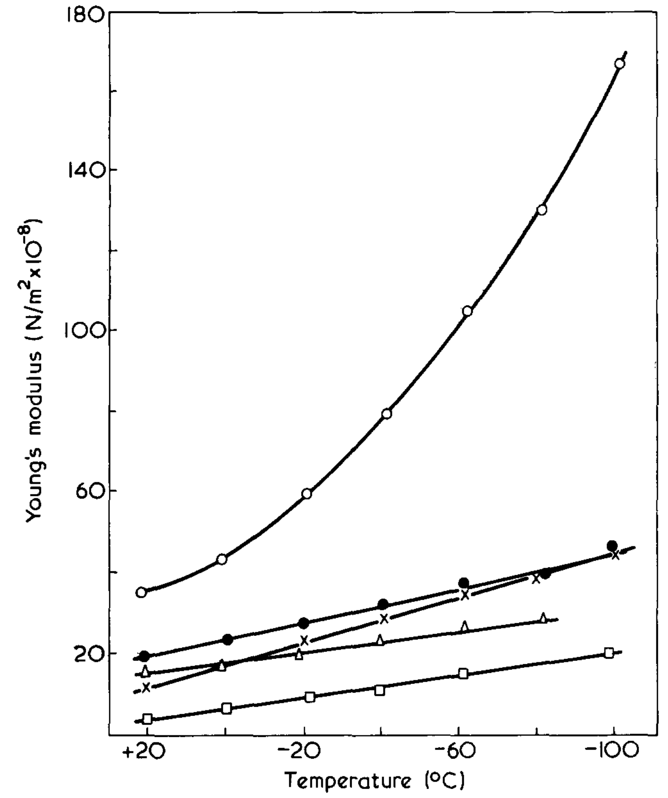


Figure 9 Young's modulus of homopolymers and copolymers at different temperatures. □, Poly(hexyl isocyanate), $[\eta] = 9$ dl/g ($M = 240\,000$); △, poly(butyl isocyanate) (as *Figure 8*); X, 20% ethyl isocyanate copolymer; ●, 44% ethyl isocyanate copolymer (as *Figure 8*); ○, 61% ethyl isocyanate copolymer

isocyanate and for an ethyl isocyanate copolymer. Both polymers show two peaks for tan δ, one in the range $-20°$ to $0°$C and one near to $100°$C, but the upper temperature of the copolymer peak is significantly higher than for the homopolymer, as might be expected for a polymer with, on the average, shorter flexible side chains. In both cases the upper peaks are rather broad, compared to those observed with conventional vinyl polymers[21] and the peak broadening is more marked with the copolymer, which could indicate a somewhat heterogenous composition[22].

Along with the broad peaks the rate of fall in the modulus with rising temperature is rather slow, compared with more conventional materials[21]. There are also significant differences in dynamic modulus between the different copolymers which appear to be closely related to the chemical composition (i.e. NCO/hydrocarbon weight ratio) as shown in *Figure 9*, There is a steady increase in modulus at all temperatures as the hydrocarbon content is decreased from hexyl to a copolymer with a high content of ethyl groups, a trend which might, of course, have been expected. Quantitatively the changes are however rather striking, especially at low temperatures.

Stress–strain curve

Particular interest attaches to the form of stress–strain curve measured with these polymers and copolymers. Examples of these are given in *Figures 10a* and *10b* for poly(n-butyl isocyanate) and for an amorphous copolymer. In *Figure 10c* we show a stress–strain curve measured in the same way on a plasticized cellulose acetate sheet which is characteristic of the uniformly extending behaviour long known to characterize the cellulosics. For example, a stress–strain curve with a similar form was found many years ago by Hermans for isotropic cellulose fibres[6]. From these results it will be clear that there are marked similarities between all the three polymers. In each case the stress–strain curve shows no peak and the stress rises continuously after yield. There is no evidence that the partly crystalline poly(n-butyl isocyanate) gives a stress–strain relation significantly different in form from that of the amorphous copolymer. Indeed all the stress–strain curves for poly(n-butyl) and poly(n-hexyl isocyanate) and copolymers were of the same shape, but there was evidence that the actual stress levels for any particular material were increased by:

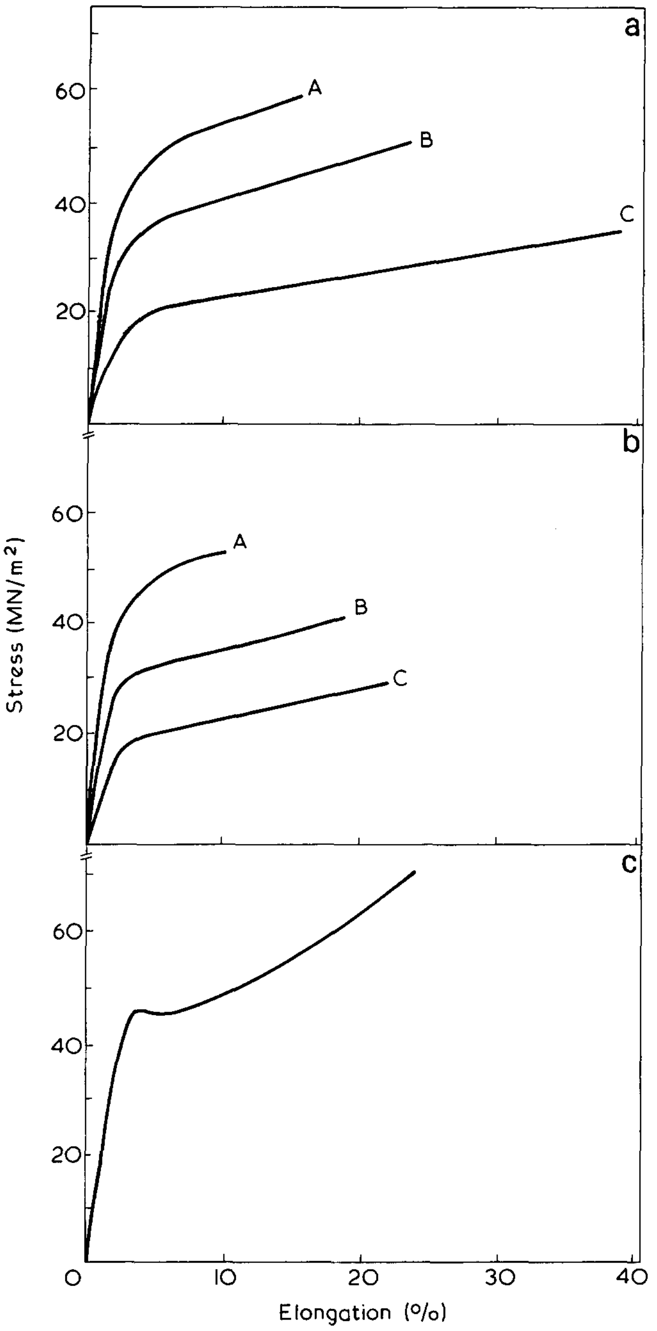


Figure 10 Stress–strain curves for isocyanate homopolymers and copolymers. (a) Homopolymers as in *Figure 8a*: A, 20° C; B, 0° C; C, 23° C; (b) copolymer as in *Figure 8b*: A, 20° C; B, 0° C; C, 23° C; (c) plasticized cellulose acetate at 23° C. Although this curve shows a small drop in engineering stress at low strains it is quite insufficient to promote necking[25] and the rapid onset of strain hardening leads to uniform extension as normally observed for cellulosics[5,6]

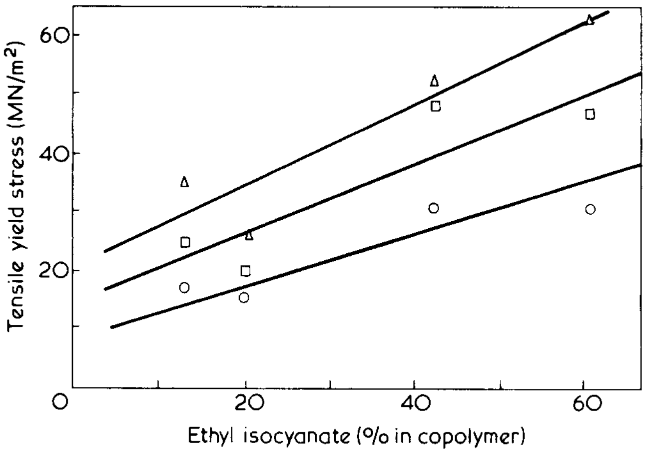


Figure 11 The relation between copolymer composition and tensile yield stress at different temperatures; ○, yield stress measured as 0.014 offset yield. ○, 23°C; □, 0°C; △, −20°C

(a) an increase in crystallinity; (b) an increase in molecular weight; (c) an increase in the NCO/hydrocarbon ratio.

The first two of these conclusions were difficult to quantify separately with complete confidence, since we found it difficult to make precise measurements of crystallinity and so to separate effects of (a) and (b). For example the density and therefore presumably the crystallinity of poly(n-butyl isocyanate) generally increased as the molecular weight was reduced. Results showing the effect of the NCO/hydrocarbon ratio on yield stress[23,24] for 4 copolymers are given in *Figure 11* and the results closely parallel the effect on modulus (*Figure 10*). These effects could not be due to crystallinity which generally decreases as the copolymer NCO/hydrocarbon ratio increases, nor could they be ascribed to changes in water absorption at the higher ratios since this effect would act in the opposing sense.

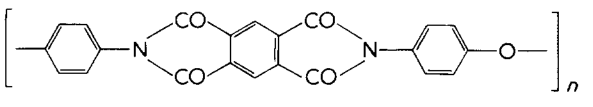
Since the form of the stress–strain curves was associated with a continuous rise in stress, without true or geometrical strain softening, the test pieces deformed uniformly without necking, according to the principle of Considere as discussed by Vincent[25]. An example of this behaviour is shown in *Figure 12* which shows a test piece extending uniformly under tension.

DISCUSSION

Polymers of the 1-nylon group clearly have a number of properties which distinguish them from most linear thermoplastics. In this respect it is unfortunate that their thermal properties are such that they cannot be easily moulded at high temperatures so that studies of their mechanical properties have to be carried out on cast films. The fact that some of the copolymers have improved thermal properties is therefore of considerable interest, although much greater improvements in this direction are clearly essential if the materials are to be processed by conventional moulding techniques.

Although the homopolymers are normally crystalline we have shown that substantially amorphous copolymers may be obtained. Most of our work has been carried out with ethyl isocyanate–butyl isocyanate copolymers but there is an indication that propyl isocyanate may be a useful constituent for amorphous materials (*Figure 5*). There is, of course, no reason to assume that the most favourable combination of monomers for making a high strength amorphous film has yet been achieved.

Particular interest attaches to the form of the stress–strain curves which are similar to those of the cellulosics[5,6] and to that of the polyimide film Kapton H[26]. With cellulose this may be related to the well-known linear configuration of the polymer chains in solution[10,27,28], and in the solid state and it seems likely that the polyimide (which has the structure shown below) behaves similarly.



Kapton H polyimide

Thus it is suggested that the highly linear conformation of the 1-nylon polymers leads to a similar form of stress–strain curve.

This conclusion would be in accordance with any model in which yielding and strain hardening were associated with the straightening of molecules in a random configuration as in rubber elasticity[5]. Where the molecules were already in a near-linear configuration, strain hardening would be expected to set in at low strains. Similar considerations apply to the treatment and arguments of Argon[29] who visualizes the yielding process in a thermoplastic as one of straightening of kinks or 'natural hinges in polymer molecules'. Thus according to either of these theories the provision of long rigid linear units in polymer chains, as in the 1-nylons, should lead to the early exhaustion of deformable bonds and so to strain hardening at low strains. On the other hand the changes in modulus and yield strength with NCO/hydrocarbon ratio are considered simply to reflect the level of intermolecular forces.

It is also tempting to explain the absence of a discontinuity in the d.s.c. curve in the same way, and although, on balance, we consider this to be likely, the limitations of the materials must be recognized. For example, the crystallinity of the butyl isocyanate homopolymer will reduce the value of ΔC_p at T_g. Against this, however, it may be noted that a discontinuity in d.s.c. or d.t.a. curves, ascribed to glass transition have been reported for conventional nylons[30] and for partly crystalline isotactic polystyrene[18]. As far as the copolymer is concerned it could also be argued that our d.s.c. result was connected with the very wide damping peak, itself resulting from copolymer heterogeneity[22].

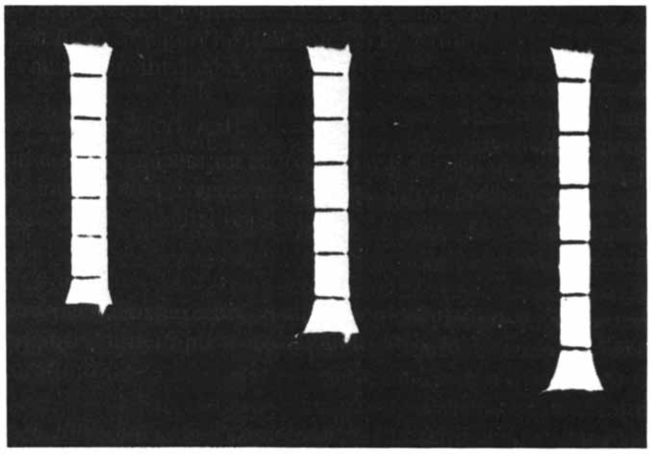


Figure 12 Photographs of butyl isocyanate copolymer at different stages in tensile test. The sample on the left is undeformed

The relation between the configurational state of a polymer above and below T_g, and the value of ΔC_p has recently been the subject of discussion[31,32] though many points remain to be cleared up. However, it would appear reasonable to assume that with a strongly linear polymer such as those described in this paper, the number of accessible configurational states will not increase excessively above T_g and so that the value of ΔC_p would be expected to be small. This is of course in line with our results. However the present authors do not know whether or not an assembly of completely straight chain molecules would be expected to show the phenomena normally associated with a glass transition.

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