Note to the Editor

Initiation of the anionic polymerization of isocyanates with sodium naphthalane

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INTRODUCTION

The polymerization of isocyanates to nylon-1 polymers was first reported by Shashoua[1] and while there has been considerable interest in the properties of such polymers[2], little attention has been given to the mechanism of the polymerization. We have studied the polymerization of cyclohexyl isocyanate (CHIC) initiated by sodium naphthalene (NaN) in tetrahydrofuran (THF), choosing reaction conditions and a monomer known to propagate slowly[3] in order to isolate the products of the initiation reaction. Sodium naphthalene may initiate anionic polymerization by either a bonding reaction with a monomer or by electron transfer; the results obtained in this study indicate that, with isocyanates, the latter mechanism predominates.

EXPERIMENTAL

All reagents were rigorously purified and handled under high vacuum conditions using breakseals. Solutions of sodium naphthalene in THF were prepared by contacting solutions of naphthalene in THF with a sodium mirror for 1 h, the resulting solutions being filtered from the sodium metal and sealed off under vacuum. Concentrations were determined by titration with standard acid. Cyclohexyl isocyanate was redistilled and stored over calcium hydride before being distilled into breakseal ampoules and weighed. Polymerizations were carried out at –78°C and 20°C for varying reaction times and were then terminated by addition of aqueous hydrochloric acid. The solvent was removed under reduced pressure and the products analysed by both gas–liquid (g.l.c.) and thin layer (t.l.c.) chromatography.

RESULTS

Addition of an excess of cyclohexyl isocyanate to sodium naphthalene resulted in the immediate disappearance of the characteristic green colour of the initiator, the solution becoming pale-yellow with a green fluroescence; when excess initiator was used, the solution remained green. Addition of aqueous acid produced a colourless solution containing a white precipitate.

IDENTIFICATION OF PRODUCTS

Preliminary studies in which water was used as a terminating agent gave complex mixtures of products some of which were believed to result from alkaline hydrolysis of some reaction products. Thereafter, all reaction mixtures were terminated with a slight excess of aqueous HCl, resulting in much simpler product mixtures. All systems contained a white precipitate after termination, soluble in chloroform but largely insoluble in ether, methanol and benzene. T.l.c. analysis showed the precipitate to be a single compound, identified as *N*,*N*^{1}-dicyclohexyl oxamide (CHOA) from analytical data (*Table 1*) and from the identical infra-red spectrum and chromatographic behaviour shown by an authentic sample of CHOA[4]. In experiments using excess initiator, g.l.c. analysis showed only one product, corresponding to CHOA. T.l.c. analysis of such systems, however, indicated another major product, a sample of which was recovered by preparative t.l.c. Infra-red analysis indicated the presence of an aromatic ring (1497 and 752 cm^{-1}), a C=O absorption at 1640 cm^{-1} and NH absorptions at 3280 and 1540 cm^{-1}. The compound was identified tentatively as a dihydronaphthalene dicarboxylic acid di-*N*-cyclohexylamide (CHNA) (1.2 and/or 1.4 isomer); elemental analysis (*Table 1*) however, consistently gave a low carbon value.

In experiments using excess monomer, only a trace of CHNA could be detected. T.l.c. indicated the presence of CHOA together with several new products, one of which could be detected on g.l.c. with a retention time slightly longer than that of CHOA. This latter component was recovered by preparative t.l.c. as a white crystalline solid and was identified as dicyclohexyl parabanic acid (CHPA) by comparison with an authentic sample[5]. Other products are under investigation of which only one could be detected on g.l.c. This was the cyclic trimer, cyclohexyl isocyanurate, which was only present when the reaction time was prolonged (e.g. run 41 below); identification was based on the coincidence of the retention time on g.l.c. with that of a sample of trimer prepared by reaction of cyclohexyl isocyanate with n-butyllithium.

Table 2 summarizes the quantitative results obtained, based on g.l.c. analysis except for the CHNA which was determined by weight after recovery from the t.l.c. plate.

DISCUSSION

It seems clear that the mechanism of initiation is predominantly that of electron transfer, producing the isocyanate radical ion which dimerizes to form the dicylohexyl oxamide dianion thus:

$$N^{\overline{\cdot}} + C_6H_{11}NCO \longrightarrow N + C_6H_{11}—\overset{-}{N}—\underset{\underset{O}{\|}}{C}\cdot$$

Table 1 Characterization of products

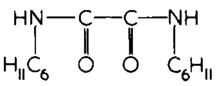
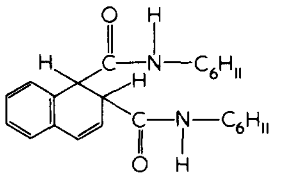
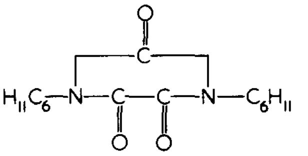
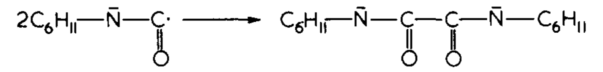
Compound			C %	H %	N %	Molecular Weight	M.p. °C
 $\underset{H_{11}C_6}{HN}-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-\underset{C_6H_{11}}{NH}$	(CHOA)	Calculated	66.7	9.5	11.0	252	273^4
		Authentic compound	67.0	9.5	11.1	–	273-4
		Isolated compound	67.2	9.5	11.0	251	273-4
	(CHNA)	Calculated	75.7	8.4	7.4	380	–
		Isolated compound	73.8	8.3	7.1	412	–
	(CHPA)	Calculated	64.7	7.9	10.1	278	$174\text{-}5^5$
		Authentic compound	65.0	7.9	9.9	–	175-6

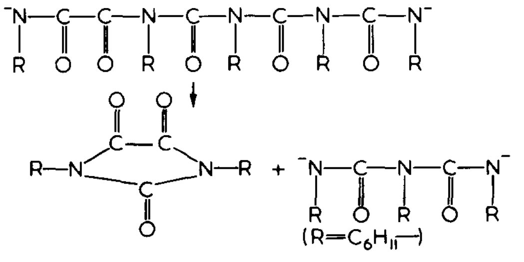
Table 2 [a] Yields of products

Run No.	T°C	Time (min)	CHIC g. (mole x 10^2)	NaN (mole X 10^2)	Products CHOA g. (%)	CHPA g. (%)	CHNA g. (%)
38	20	60	1.32 (1.05)	2.60	0.99 (75.3)[c]	none	0.44 (22)[c]
40[b]	20	60	0.87 (0.69)	1.47	0.67 (77.2)[c]	none	–
42	20	10	1.35 (1.08)	0.47	0.42 (71.8)[d]	0.12 (17.7)[d]	–[e]
41	20	900	1.60 (1.28)	0.44	0.03 (5.0)[d]	0.35 (58.0)[d]	–[e]
43	–78	10	1.52 (1.22)	0.24	0.26 (85.4)[d]	0.03 (9.8)[d]	–[e]

[a] Volume of solution ~100 ml. [b] Sodium biphenyl used. [c] Yields based on monomer [d] Yields based on NaN, assuming 2NaN form 1 oxamide unit. [e] Trace


$$2C_6H_{11}-\bar{N}-\underset{\underset{O}{\|}}{C}\cdot \longrightarrow C_6H_{11}-\bar{N}-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-\bar{N}-C_6H_{11}$$

Even when excess initiator was used (runs 38 and 40), the major product was the oxamide dianion, using either sodium naphthalene or sodium biphenyl as initiator. Using excess monomer allows the oxamide dianion to propagate and at prolonged reaction times, little CHOA can be recovered. The propagation reaction presumably gives rise to a series of oligomers, some of which cyclize to produce CHPA thus:–



Thus at –78°C, 95% of the initiator used can be accounted for in products formed *via* electron transfer initiation, in agreement with the fact that only trace amounts of naphthalene containing species could be detected. Indeed, it seems likely that when excess monomer is used, the initiation is almost entirely by electron transfer, the remaining oxamide units being present in as yet uncharacterized linear oligomers.

The lack of products containing naphthalene bonded to isocyanate units when excess monomer was used implies that direct addition to cyclohexyl isocyanate to the naphthalene radical ion is much slower than the electron transfer process and therefore that the CHNA formed using excess initiator is more likely to have formed from coupling of the naphthalene and isocyanate radical ions, followed by monomer addition. Such a mechanism was considered for the potassium naphthalene–octamethyl–cyclotetrasiloxane reaction[6] though it was thought to be less likely than the mechanism usually proposed, for example, with ethylene oxide[7], carbon dioxide[8] and formaldehyde[9]. Although, the results show a considerable similarity to those of the sodium naphthalene–diphenyl carbodi-imide system where electron transfer occurs as well as an analogous cyclization process[10]. Preliminary studies with n-butyl isocyanate indicate that electron transfer again predominates, suggesting that this result is general for all isocyanates; it is noteworthy that although carbon dioxide and isocyanates have similar cumulative bonds, they react with sodium naphthalene in entirely different ways.

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Letter

Deformation of PMMA samples containing a stress-raising flaw

It is well established that yield in glassy amorphous polymers occurs either by craze formation or shear deformation. Extensive reviews of work on the conditions for craze and shear yielding have been made by Kambour[1] and Bowden[2] respectively. Crazing and shear deformation can occur independently and exclusively, or simultaneously, depending on the test conditions in general, but in particular on the nature of the local stress field.

We are examining the deformation of polymeric glasses in uniaxial compression with samples containing a centrally positioned stress-raising flaw. Previously published work by Bevan[3] has shown that whilst crazing requires a state of hydrostatic tension, such states can exist locally when a specimen with a suitable flaw is deformed nominally in compression, or when it is unloaded after compressive yielding. The present investigation deals with aspects of shear band deformation, craze and crack formation not reported previously.

Experimental

PMMA (ICI 'Perspex') samples of nominal dimensions 20 x 20 x 6 mm containing a centrally-drilled 2 mm diameter hole were annealed, between smooth aluminium plates, in air at 95°C for more than 1 h and then cooled to room temperature at a rate of about 10°C/h. Samples were subsequently subjected to applied uniaxial compression at ambient temperature between the dies of an Instron machine. Tests were conducted at a strain rate of $4.2 \times 10^{-4} s^{-1}$. The results reported here were obtained with no lubricant at the interfaces, but separate tests using Teflon tape showed the same deformation characteristics.

The onset of residual birefringence in the samples was determined from a large number of interrupted compressive tests where samples subjected to various strains were rapidly unloaded and viewed in an adjacent polariscope.

Some tests were done on samples with differing surface conditions of the hole. These were obtained by varying the drilling conditions and also by polishing the internal hole surface with a cylindrical roll of 600 grade emery paper. The same deformation features are observed irrespective of the surface conditions of the hole. The results reported here were obtained on unpolished holes.

Results

The nominal stress–nominal strain graph obtained for our samples shows a departure from linearity at 2.8% ϵ and exhibits a load maximum at 9.5% ϵ, similar to results reproduced by Bowden[2] for PMMA in uniaxial compression. Diffuse shear zones were distinguished from birefringence observations. These zones propagate symmetrically from the hole across the sample at an angle of about 50° to the compressive axis and appear to reach the edges of the sample as the stress–strain graph becomes non-linear. Samples unloaded at this point showed no residual birefringence several hours later. Remnant birefringence was associated with the initiation and growth of 'broad diffuse shear bands'. These shear bands initiated at the hole at about 6% ϵ within the established shear zones. The bands subsequently propagated through the zones and were observed to reach the sample edge at about the load maximum. Specimens showed a slight thickening along the shear bands due to the surface of the shear band bulging outwards symmetrically from the surface about the band propagation direction. This type of 'broad diffuse shear band' is quite different to the sharply defined shear bands observed in polystyrene[4,5] and polycarbonate[6].

When samples were unloaded some of them were observed to contain three mutually perpendicular discontinuities, which are either craze- or crack-like in nature. These were designated C_L, C_B and C_U as shown schematically in *Figure 1*. C_L and C_U have been reported previously[3]. C_L formed during loading at strains of between 6 and 8%. C_B, which we have called a 'butterfly' discontinuity, also occurred during loading at a strain of about 9 or 9.5%. The unloading discontinuity C_U was always present on samples unloaded from about 7%. Each type of loading feature can occur on either or both sides of the hole and we have observed samples containing only C_L, only C_B, and both types simultaneously.

The initiation and propagation of C_L, C_U and C_B have been observed with an optical microscope. C_L and C_B appear to initiate as crazes, rather than cracks, but rapidly break down into cracks. The initiation of 'craze' C_L is often followed by its propagation as a crack, signified by an audible click.

Scanning electron microscope studies of sections of