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New polyurethanes with conjugated triple bonds

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Summary

Urethane polymers possessing two conjugated -C≡C- triple bonds per repeating unit are synthesized. Polyurethanes are characterized by their infrared absorption spectra, UV abrsorption spectra and elementel analysis. Their molecular weights and limit intrinsic viscosities are determined. Solutions of these polymers in various solvents do not show any reactivity when exposed to light or heat. However the solid polyurethanes and solvent cast polyurethane films obtained from trimethyl hexamethylene diisocyanate, and isophoron diisocyanate quite rapidly develop red - brown colour on annealing at elevated temperatures, below their melting point. During this process the polymers themselves and solvent cast polymer films become insoluble in any of the solvents. Their IR and UV absorption spectra before and after annealing are examined and the band gaps are calculated from the spectral data.

Introduction

The topochemical polymerization of conjugated diacetylenes has become a promising tool of preparative polymer chemistry in recent years. The solid state diacetylene polymerization reaction was first characterized by Wegner and applied to a wide variety of monomers (1-8).

It was also shown that some polyesters, polyurethanes and various other polymers containing conjugated triple bonds undergo a crosslinking through the same diacetylene reaction mechanism (9-11).

The term macromonomer was used to describe the original diacetylenic bond containing polymer and the crosslinking reaction taking place within the polymer chains was named as cross - polymerization. It was a systematic polymerization of the diacetylene units (as indicated in Fig.1.) , which was different from the more familiar random crosslinking that many polymers undergo when exposed to heat or light. In our case the resultant side groups are actual polymer chains connecting the poly (diacetylene) conjugated backbones in a networklike structure. Recently this approach has been extended to segmented copolymers in which the cross - polymerization reaction can be restricted to phase - separated domains, containing the diacetylene groups (12-13).

While a number of different macromonomers have been synthesized and subsequently cross-polymerized a detailed investigation of the structure-property relationships in these materials has not emerged. It is expected that with the right combination of structure and molecular organization, these materials would exhibit interesting properties and novel mechanical

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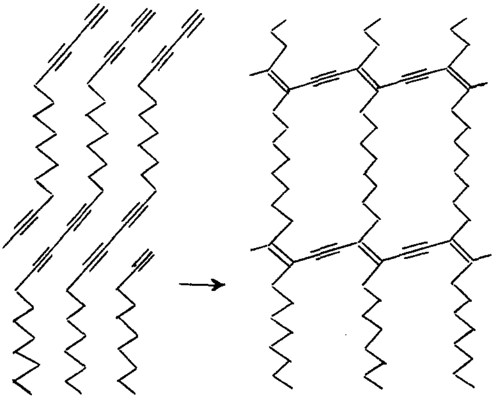


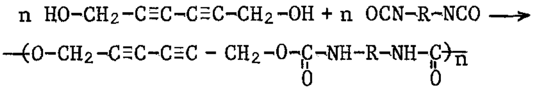
Figure 1. Model of cross-polymerization reaction

behaviour. The properties of these polymers could also be readily modified by controlling the extent of cross-polymerization of the diacetylene groups.

In this work three new polyurethane macromonomers are prepared. The diol : diisocyanate ratio is taken as "1" in order to obtain a chain extension reaction. In all of the macromonomers the same diol (2,4 hexadiin 1,6 diol) is used but the diisocyanates have different characters.

The first one is aliphatic, trimethyl hexamethylene diisocyanate and the corrosponding polymer named as TMDI, the second one is saturated cyclic, isophoron diisocyanate, and the corresponding polymer name IPDI, and the third one is an aromatic diisocyanate, tolulyn diisocyanate and the polymer named as TDI.

The polyurethane macromonomer formation reaction can be represented as follows,



$$n\ HO-CH_2-C\equiv C-C\equiv C-CH_2-OH + n\ OCN-R-NCO \longrightarrow$$

$$-\!\!\left(O-CH_2-C\equiv C-C\equiv C - CH_2-O-\underset{\underset{O}{\|}}{C}-NH-R-NH-\underset{\underset{O}{\|}}{C}\right)_{n}$$

At the end of the reaction period the chain end is capped by $-OC_2H_5$ group by adding ethanol to the reaction mixture. Our R groups are shown in Tab.1.

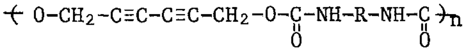
The molecular weights and the limit intrinsic viscosities of macromonomers are investigated. Their cross polymerization temperatures are determined. Macromonomers and annealed (cross polymerized) macromonomer film's IR and UV spectra are examined and the effect of annealing (cross polymerization) on polymer properties is observed.

Experimental

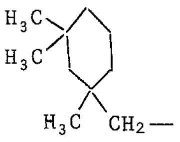
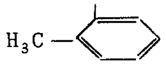
Materials

2,4 Hexadiyne-1,6 diol is a product of Fluka A.G. It is dried at 60°C for 4 hours at reduced pressure before use. Trimethylhexamethylene-diisocyanate is a product of Merck A.G. and isophoron-diisocyanate, tolulyn-2,4 diisocyanate, dibutyltin-dilaurat are products of Fluka A.G. They are used without further purification. Triethylamine and n.n-dimethylformamide (DMF) are freshly distilled prior to use.

Table 1. The R groups in polyurethane macromonomers.



$$-\!\!\left(O-CH_2-C{\equiv}C-C{\equiv}C-CH_2-O-\underset{\underset{O}{\|}}{C}-NH-R-NH-\underset{\underset{O}{\|}}{C} \right)\!\!-_n$$

Macromonomer	R
TMDI	$-CH_2-C(CH_3)_2-CH_2-CH(CH_3)-(CH_2)_2-$
IPDI	
TDI	

Procedure

20 mmol diol is dissolved in 20 ml DMF at room temperature and 20 mmol diisocyanate is added quickly to the diol solution. 0,1 ml triethylamine and 20 mg dibutyltin-dilaurat are added successively. The whole mixture is kept under dry nitrogen atmosphere. The reaction mixture is mixed vigorously at room temperature for 1 hour and then at 85°C for 2. hours. At the end of this period 5 ml ethanol is added and the mixture is poured into a 200 ml of water. The polyurethane macromonomers thus formed, are filtered through a sintered crucible washed several times with water and dried in vacuo at room temperature.

Characterization and Properties

All polymers are found to be light sensitive in different proportions. For this reason they are stored in coloured bottles in dark.

The results of elementel analysis of these three macromonomers are as follows,

TMDI	$(C_{17}\ H_{22}\ N_2\ O_4)_n$	Calcd.	C 63,69	H 7,49	N 8,74
		Found.	C 63,37	H 7,97	N 9,13
IPDI	$(C_{18}\ H_{24}\ N_2\ O_4)_n$	Calcd.	C 64,74	H 7,19	N 8,39
		Found.	C 63,03	H 7,34	N 7,91
TDI	$(C_{15}\ H_{10}\ N_2\ O_4)_n$	Calcd.	C 63,38	H 4,25	N 9,85
		Found.	C 64,53	H 5,30	N 10,56

The IR spectra of macromonomers are recorded using FTIR-Bruker spectrophotometer in KBr pellet form and solvent cast films. The UV spectra of macromonomers are recorded using Shimadzu Double Beam spectrophotometer in solution and film form. In the IR spectra of the macromonomers (KBr pellet form) peaks around 3300 cm^{-1} are observed in all of them. This absorption is due to the -NH- stretching in the -NH-CO- group of the macromonomer. They are appeared at 3334 cm^{-1} (TMDI), 3340 cm^{-1} (IPDI) and 3377 cm^{-1} (TDI). The first and second amid groups are also appeared at 1713, 1537 cm^{-1}(TMDI), 1720, 1527 cm^{-1}(IPDI) and 1776, 1510 cm^{-1}(TDI),

Table 2. Cross-polymerization temperatures, intrinsic viscosisies, |η|, number awerage molucular weights, M_n, and the number of repeating units (n) in each macromonomer.

Macromonomer	Temp. °C (colour change)	|η| dl/gr	M_n	(n)
TMDI	50-70 pale yellow-red brown	(1)0,102 (2)0,145	21800 65300	68 204
IPDI	90-100 pale yellow-red brown	(1)0,191 (2)0,478	12500 37500	37 113
TDI	up to 200°C no change			

Peaks due to diacetylere group are appeared at 2258 cm^{-1} (TMDI), 2260 cm^{-1} (IPDI), 2218 cm^{-1} (TDI) (2). The UV spectra of macromonomers in dioxane solution give a single peak λ_{max}=250 nm (TMDI), λ_{max}=240 nm (IPDI) which are characteristic of diacetylene cromophore (11,14). In the UV spectra of solvent cast film of TMDI max absorption is observed at λ_{max}=315 nm.

Since TDI becomes partly insoluble within a limited exposure do daylight its molecular weight could not be determined. The limit intrinsic viscosities of other macromonomers, TMDI and IPDI, are measured in dioxan at 35°C using an Ubbelohde-type viscometer. Number average molecular weights of macromonomers (TMDI and IPDI) are measured by membran osmometer (Knauer) in dioxan solution at 35°C. The results are given in Tab.2. The macromonomers TMDI and IPDI are soluble in dioxane, acetone, DMF and THF but not soluble in benzene, toluene and chlorinated solvents.

Pale yellow solutions of macromonomers in these solvents do not polymerize when heated or irradiated with UV light. However the macromonomers themselves quite rapidly develop a red-brown colour when heated up to a certain temperature below their melting points or irradiated with UV light and become insoluble in all of the solvents (cross-polymerization). Visual observation of thermal changes are made by heating the polymer sample in capillary tube with a melting point apparatus. The results are given in Tab.2. The solvent cast films of macromonomers from dioxane also changed their yellow colour to red-brown when heated up to the temperatures cited in Tab.2. and become insoluble in all of the solvents. In the IR spectrum of cross polymerized films the similar functional groups are observed except the diacetylane peak which was at 2260 cm^{-1} disappeared due to cross polymerization. The UV spectrum of cross polymerized films give again a single shifted maximum, for example in TMDI case shifted from λ_{max}=315 nm to λ_{max}=345 nm.

The band gap calculated from spectral data for IPDI macromonomer film found to be Eg = 3.5 e.v. and in cross polymerized film (heated at 100°C overnight in N_2 atms) Eg = 3,3 e.v. (15). For TMDI the band gap of macromonomer found to be Eg ≈ 3,3 e.v. and decreased up to Eg = 2,67 e.v. (heated at 100°C overnight) due to cross polymerization. The band gap values have not changed upon further annealing.

Discussion

Diacetylenic polyurethanes $\left(\!-R-C\equiv C-C\equiv C-R-\!\right)_n$ which the R groups have different characters are synthesized in this study.

In TMDI and IPDI the diacetylene groups are somehow shielded by $-CH_3$ groups in the molecule. For this reason these macromonomers are almost stable in daylight at some extent. However in TDI due to the rigid nature of both diacetylene and phenyl groups, diacetylene groups are not shielded, and TDI changed colour easily from yellow to dark yellow (pale brown) within a limited exposure to daylight and became insoluble in all of the solvents. In the TMDI and IPDI case it was necessary to heat or irradiate them in order to cross polymerize the macromonomer.

In the IR studies of macromonomers and annealed (cross polymerized) films the similar peaks are observed. Only the diacetylene peak dissepeared as expected due to cross-polymerization reaction.

In the UV studies the band gap value of IPDI cross polymerized films appeared to be higher than TMDI films. More straightforward chain nature of TMDI is probably responsible for its lower band gap value.

On further studies dopping TMDI cross polymerized films with different dopants and determining conductivity values are in progress.

References

1. Wegner, G., Z. Naturforsch 24b, 824 (1969)
2. Wegner, G., Makromol Chem. 134,219-229 (1970)
3. Wegner, G., Makromol Chem. 145, 85-94 (1971)
4. Wegner, G., Makromol Chem. 154, 35-48 (1972)
5. Takeda, K., Wegner, G., Makromol Chem. 160, 349-353 (1972)
6. Baughman, R.H., Yee, K.C., J. Polym. Sci. Polym. Chem. Ed. 12. 2467-2475 (1974)
7. Yee, K.C., Chance, R.R., J. Polym. Sci. Polym. Chem. Ed. 16, 431-441 (1978)
8. Wenz, G., Wegner, G., Makromol Chem. Rapid. Commun. 3, 231-237 (1982)
9. Thakur, M., Lando, J.B., Macromolecules 16, 143-146 (1983)
10. Day, D., Lando, J.B., J. Polym. Sci. Polym. Lett. Ed. 19, 227-233 (1981)
11. Patil, A.O., Deshpande, D.D., Talwar, S.S., Biswas, A.B., J. Polym. Sci. Polym. Chem. Ed. 19, 1155-1166 (1981)
12. Rubner, M.F., Macromolecules 19, 2114-2128 (1986)
13. Rubner, M.F., Macromolecules 19, 2129-2138 (1986)
14. Armitage, J.B., Whiting, J. Chem. Soc. 2005 (1952)
15. Faiz, M., Ph.D. Thesis The Chemistry and Molecular Sciences, The University of Sussex U.K. (1987)

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