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Polymerizations by 1,3-Dipolar Cycloaddition Reactions. VI. Syntheses of Polyurethans with Isoxazoline or Isoxazole Linkages

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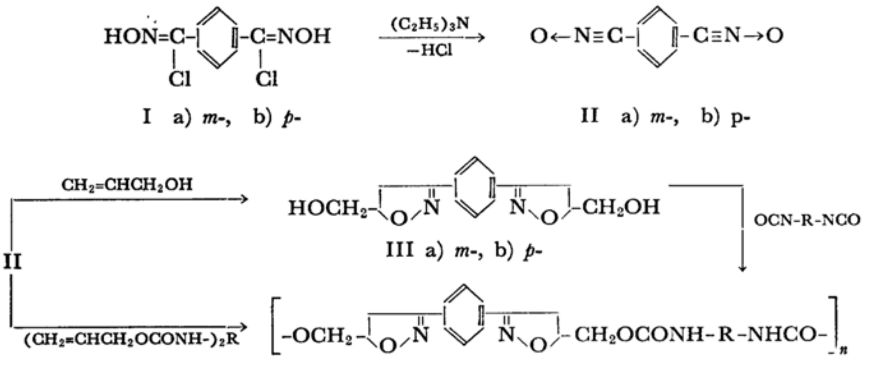
Polyurethans with isoxazoline or isoxazole linkages in the polymer main chains were prepared by polyadditions of diols with isoxazoline or isoxazole rings and diisocyanates. The diols were prepared by 1,3-dipolar cycloaddition reactions of tere- and iso-phthalonitrile di-*N*-oxides with allyl or propargyl alcohol. Polyurethans of the same structures were also prepared by 1,3-dipolar polycycloadditions of the nitrile oxides with bisallyl or bispropargyl carbamates.

The 1,3-dipolar cycloaddition reaction, first defined and extensively studied by Huisgen and his coworkers,[1] is an interesting method of synthesizing heterocyclic compounds. The high yields of the reaction products have prompted several recent investigations of the syntheses of the polymers with heterocyclic rings by this reaction. We ourselves have already reported[2] the preparation of new diols with heterocycles by the reactions of tere- and isophthalonitrile di-*N*-oxides with allyl or propargyl alcohol. The present paper is concerned with the preparation of new types of polyurethans with isoxazoline or isoxazole rings in their polymer main chains from those diols, and with the preparation of the polymers of the same structures by 1,3-dipolar polycycloadditions. The generalized reaction scheme and the structures of the polymers are shown below:

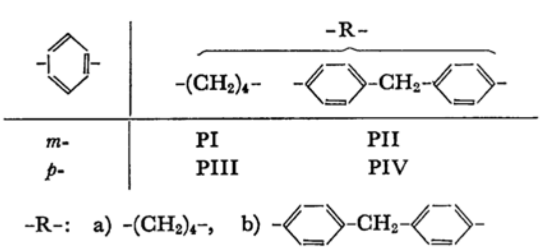


I a) *m*-, b) *p*-

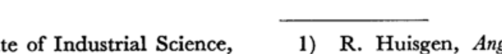
II a) *m*-, b) p-

III a) *m*-, b) *p*-

V



	-(CH₂)₄-	-C₆H₄-CH₂-C₆H₄-
m-	PI	PII
p-	PIII	PIV



-R-: a) $-(CH_2)_4-$, b) $-C_6H_4-CH_2-C_6H_4-$

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1) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); R. Huisgen, R. Grashey and J. Sauer, in "The Chemistry of Alkenes," Interscience, New York (1963), p. 806.

2) Y. Iwakura, S. Shiraishi, M. Akiyama and M. Yuyama, This Bulletin, **41**, 1648 (1968).

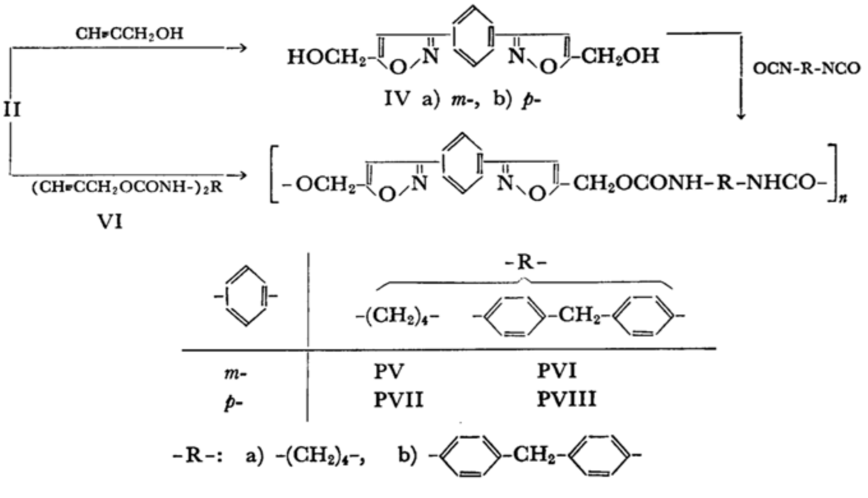


Table 1. Diols with isoxazoline or isoxazole rings

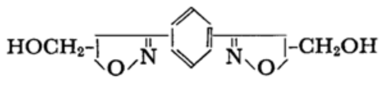
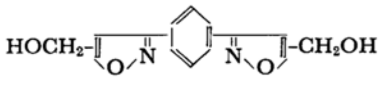
Diol		Yield (%)	Mp (°C)	Anal. (%)		
				C	H	N
	*m*-IIIa	72	127—135	60.51	5.91	10.12
	p-IIIb	74	227—228	60.44	5.87	10.16
	Calcd for $C_{14}H_{16}N_2O_4$:			60.86	5.84	10.14
	*m*-IVa	40	154—155	61.60	4.53	10.36
	p-IVb	58	225—226	61.52	4.43	10.30
	Calcd for $C_{14}H_{12}N_2O_4$:			61.76	4.44	10.29

Table 2. Polyurethans prepared by polyaddition reactions

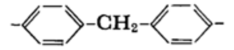
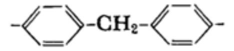
Polymer	Solvent (mmol/m*l*)	React. time (hr)	React. temp. (°C)	η_{inh}	PMT (°C)	N anal. (%)	
						Found	Calcd
PI	Anisole(5/10)	2	Reflux	0.39[a)]	180—198	13.42	13.46
PII	Anisole(5/10)	2	Reflux	0.50[a)]	210—217	11.43	10.64
PIII	HMPA(5/10)	8	120	0.19[b)]	260—267	14.06	13.46
PIV	HMPA(5/10)	30	80	0.22[b)]	294—297	10.66	10.64
PV	Anisole(5/10)	2	Reflux	0.72[a)]	194—207	13.77	13.58
PVI	Anisole(5/10)	4	Reflux	0.32[a)]	200—228	10.60	10.72
PVII	DMAc(2.5/5)	22	120	0.11[b)]	235—240	14.01	13.58
PVIII	DMAc(5/10)	28	100	0.17[b)]	288—290	10.60	10.72

a) 0.5 g/100 m*l* of DMF, at 30°C. b) 0.5 g/100 m*l* of DMSO, at 30°C.

Diols with isoxazoline rings, 3,3′-(*m*- and *p*-phenylene)bis(5-hydroxymethyl-2-isoxazoline) (IIIa and IIIb), and those with isoxazole rings, 3,3′-(*m*- and *p*-phenylene)bis(5-hydroxymethylisoxazole) (IVa and IVb), were prepared by 1,3-dipolar cycloaddition reactions of iso- and tere-phthalonitrile di-*N*-oxides with allyl alcohol and with propargyl alcohol respectively in tetrahydrofuran (THF) solution at room temperature. They were also prepared from the corresponding hydroxamic chlorides and the alcohols mentioned above in THF, in the presence of triethylamines as a hydrogen chloride acceptor. IIIa and IIIb each have two asymmetric carbons to which a hydroxymethyl group attaches; therefore, they should each have two isomers, *meso* and *dl*. Indeed, the melting point of IIIa shows the broad range of 127—135°C, suggesting that it may be a mixture of the two isomers. However, attempts to separate the diastereomers have been unsuccessful. These diols are summarized in Table 1.

The polyaddition reactions of the diols described above were conducted with tetramethylene diisocyanate and with 4,4′-diisocyanatodiphenylmethane to give new types of polyurethans. The polyaddition conditions and the results are shown

TABLE 3. BISALLYL AND
X-OCONH-R-

	Compound		Yield (%)	Recryst. solvent
	X	R		
Va	$CH_2=CHCH_2-$	$-(CH_2)_4-$	78.3	50%-CH_3OH
Vb	$CH_2=CHCH_2-$		88.5	95%-CH_3OH
VIa	$CH\equiv CCH_2-$	$-(CH_2)_4-$	91.0	Benzene
VIb	$CH\equiv CCH_2-$		93.0	50%-CH_3OH

in Table 2. The diols with a *m*-phenylene link, IIIa and IVa, gave relatively-high-molecular-weight polymers with inherent viscosities of 0.3—0.7 (0.5 g/100 m*l* of DMF), while the diols with a *p*-phenylene link, IIIb and IVb, gave rather-lower-molecular-weight polymers with inherent viscosities of 0.11—0.22. The latter diols were less soluble in anisole; moreover, the polyurethans derived from them were also insoluble in the solvent. For that reason, the polymer formed precipitated from the reaction mixture before a high degree of polymerization was attained. Some other solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), and hexamethylphosphoramide (HMPA) were also used as reaction media, but high-molecular-weight polymers were not obtained in such cases.

The polymers derived from IIIa and IVa are soluble in such polar solvents as DMF, DMAc, DMSO, and HMPA, but are insoluble in methanol, acetone, THF, anisole, and benzene. Those derived from IIIb and IVb are soluble in DMSO, but are only partly soluble in DMF and DMAc.

Polyurethans of the same structures were also obtained by 1,3-dipolar polycycloadditions of the nitrile oxides with a bisallyl carbamate or with a bispropargyl carbamate. These difunctional unsaturated carbamates were prepared by the reaction of the diisocyanates described above with allyl or propargyl alcohol. The carbamates are summarized in Table 3.

The 1,3-dipolar polycycloadditions were carried out in a THF solution by heating under reflux. When isolated nitrile oxides (II) were used, the molecular weights of the polymers obtained were rather low. The inherent viscosity of the polymers was not larger than 0.2 in any case. On the other hand, relatively-high-molecular-weight polymers were obtained when hydroxamic chlorides (I) were used in the presence of triethylamine as a hydrogen chloride acceptor. This indicates that the *in situ* addition of the nitrile oxide may be favorable to the polymerization reaction. Typical conditions and the results for the polymerization reactions of hydroxamic chlorides with difunctional dipolarophiles in THF are shown in Table 4. When anisole, *o*-dichlorobenzene, *m*-cresol, or DMSO was used as the reaction medium, the results were not better than those in Table 4.

TABLE 4. POLYURETHANS PREPARED BY 1,3-DIPOLAR POLYCYCLOADDITIONS

Polymer	Time (hr)	Yield (%)	η_{inh}	PMT (°C)
PI	0.5	48	0.47[a)]	185—206
PII	1	34	0.58[a)]	196—209
PIII	1	86	0.17[b)]	242—256
PIV	2.5	88	0.23[b)]	268—271
PV	1.5	64	0.25[a)]	180—208
PVI	1	86	0.23[a)]	195—217
PVII	2	70	0.22[b)]	250—260
PVIII	2	95	0.23[b)]	274—278

a) 0.5 g/100 m*l* of DMF, at 30°C.
b) 0.5 g/100 m*l* of DMSO, at 30°C.

The infrared spectra of the polymers obtained here coincided closely with the corresponding polymers obtained by the polyadditions described above. Their polymer melt temperatures (PMT) also exhibited similar values. As expected, the melting points of the polymers in this series are affected mostly by whether the heterocyclic units are linked by *m*-phenylene or *p*-phenylene groups. The melting points of PI, PII, PV, and PVI, all of which are *m*-phenylene-linked, are in the range of 180—210°C, whereas those of PIII, PIV, PVII, PVIII, which are *p*-phenylene-linked, are in the 250—280°C range.

Among the polymers prepared in this investigation, those with inherent viscosities above 0.3, which are exclusively *m*-phenylene-linked, can all be casted to a self-supporting film from a DMF solution. The film casted from the higher-molecular-weight polymer was tough and transparent.

Experimental

Preparation of the Diols. All of the diols were prepared by the reaction of the corresponding nitrile oxides with allyl alcohol and with propargyl alcohol in

BISPROPARGYL CARBAMATES

NHCOO-X

Mp (°C)	Anal. (%)					
	Found			Calcd		
	C	H	N	C	H	N
76—77	56.33	7.84	11.00	56.23	7.87	10.93
123—124	68.70	6.23	7.92	68.83	6.05	7.65
84—85	57.00	6.56	11.13	57.13	6.39	11.11
163—164	69.74	5.22	7.73	69.60	5.00	7.73

a THF solution at room temperature. They were purified by recrystallization from aqueous methanol in all cases. The analytical data are shown in Table 1. A typical example is as follows: Into a stirred solution of 4 g (0.069 mol) of allyl alcohol in 75 m*l* of THF, there were added, portion by portion, 4.7 g (0.029 mol) of isophthalonitrile di-*N*-oxide (IIa). After the reaction mixture had been let stand overnight, the solvent was evaporated under reduced pressure. The residue was recrystallized twice from 50%-aqueous methanol to give 5.7 g (72% of the theoretical amount) of colorless crystals of IIIa, mp 127—135°C. Further recrystallization did not change the melting point.

Polyaddition of the Diols with the Diisocyanates. A typical example is as follows: 1.380 g (0.005 mol) of IIIa and 0.700 g (0.005 mol) of tetramethylene diisocyanate were placed in 10 m*l* of anisole, and the mixture was stirred and then gently heated to reflux. After the mixture became a clear solution, 15 mg (2.5×10^{-5} mol) of dibutyltin dilaurate was added to the solution as a catalyst. Stirring and heating were continued for 2 more hours. The resinous product separated from the solution and deposited at the bottom of the vessel. After the reaction mixture had cooled, the resinous product was separated and dissolved in DMF. The DMF solution was filtered with a glass funnel and poured into methanol to precipitate the polymer, PI. It was gathered by filtration, washed methanol, and dried at 60°C *in vacuo*. The analytical sample was obtained by treating the polymer with boiling methanol to remove the DMF occuluded in it.

The other polymers were prepared by a similar procedure.

Preparation of the Bisallyl Carbamates and Bispropargyl Carbamates. Bisallyl carbamates were prepared by the reaction of allyl alcohol with the corresponding diisocyanate in petroleum ether, and bispropargyl carbamates were prepared from propargyl alcohol and the diisocyanates in benzene. As the reaction proceeded, in each case the carbamate formed precipitated out of the reaction mixture. When tetrahydrofuran was used as the reaction medium, the solvent was evaporated to obtain the product as a solid. A typical example is as follows: Eight grams of tetramethylene diisocyanate (0.057 mol) and 7 g (0.12 mol) of propargyl alcohol were placed in 20 m*l* of THF, and the mixture was left to stand overnight. The subsequent evaporation of the solvent left a solid. It was recrystallized from benzene to give 12.8 g (91%) of colorless needles of VIa, mp 84—85°C.

The analytical data and the solvents of recrystallization are summarized in Table 3.

Procedures of the 1,3-Dipolar Polycycloadditions. A solution of a dihydroxamic chloride (I) (0.0025 mol) and a bisallyl or bispropargyl carbamate (V or VI) (0.0025 mol) in 5 m*l* of THF was heated under reflux with stirring. To the solution there was then added, drop by drop, 0.006 mole of triethylamine in 5 m*l* of THF. A white precipitate thereupon began to be deposited. The precipitate formed at the earlier stage of the reaction was triethylammonium chloride. The mixture was stirred for an hour, and then the solid deposited was gathered by filtration and dissolved in DMSO. The DMSO solution was filtered with a glass funnel and poured into methanol to precipitate the polymer. It was collected by filtration, washed with methanol, and dried under vacuum.

When other solvents were used as the reaction media, the reaction temperature was kept at a temperature in the range between room temperature and 70°C. The other procedures were similar to those mentioned above.

The polymerization procedures in which isolated nitrile di-*N*-oxides (II) were used as the starting components were the same as those described in a previous paper.2)