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Formation of poly(urethane-isocyanurate) networks from poly(oxypropylene)diols and diisocyanate

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Summary

Reaction conditions leading to the smallest amount of unreacted isocyanate groups for the preparation of poly(urethane-isocyanurate) networks based on 2,4-tolylene diisocyanate and α,ω-dihydroxypoly(oxypropylene) (M_n = 425–4000) were found. A tertiary amine, POLYCAT* 41, was used as a cyclotrimerization catalyst. The networks were prepared by prepolymer two-stage technique. The content of isocyanate groups in the prepolymers and networks was determined by potentiometric titration. Model reactions in 1,4-dioxane were used for the estimation of possible reaction intermediates during poly(urethane-isocyanurate) synthesis.

Introduction

Polyurethane networks are of great practical and theoretical importance (as model ones) due to simple build-up of structure from hydroxyl and isocyanate. The systems based on poly(oxypropylene)triols and diisocyanate or poly(oxypropylene) diols and triisocyanate were used in testing theories of formation and elastic behaviour of polymer networks [1,2]. While networks in which hydroxyls are in excess are stable and the formation of networks with excess of isocyanates can be accompanied by a number of chemical side reactions owing to a high reactivity of isocyanate groups. Urethane, allophanate, urea, biuret, isocyanurate, uretidinedione, carbodiimide and oxazolidone groups can be formed [3]. This fact considerably complicates the preparation of NCO endcapped polymers and networks with defined structure and properties. However, difficulties need not be caused only by a high isocyanate reactivity. Hydroxyl containing materials sometimes can include traces of substances acting as catalysts for isocyanate cyclotrimerization (e.g. metal acetates). These substances were found in some commercial poly(oxyethylene)diols [4]. It was discovered that there exists a threshold concentration of the catalyst, below which cyclotrimerization is not observed (cf. Ref. 4, Fig. 6).

Our earlier investigations [5,6] on model reactions of phenyl isocyanate (in excess), 1-butanol or butyl-N-phenyl urethane and cyclotrimerization catalysts (quaternary ammonium salt, organic-acid salt, tertiary amine) at 30–50°C in 1,4-dioxane and in the presence of traces of water revealed that besides isocyanurate also urea, urethane, biuret and allophanate are formed. The concentration of the unreacted isocyanate depends on the type of catalyst, time and temperature. It was also found that there remains more isocyanate in the presence of urethane than in its absence. Biuret and allophanate are not stable and they decompose in the presence of catalyst in time.

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In this paper we try to find reaction conditions for optimum preparation of poly(urethane-isocyanurate) networks based on 2,4-tolylene diisocyanate and poly(oxypropopylene)diols of various molecular weights. The other aim was to calculate the concentrations of various groups in networks by combining the data on unreacted isocyanate groups and results of model reactions.

Experimental

Materials

2,4-Tolylene diisocyanate (TDI; Fluka) was purified by distillation (b.p. 120°C at 2100 Pa). Its purity, 99.9%, was determined by potentiometric titration.

α,ω-Dihydroxypoly(oxypropylenes) (PPD) of nominal molecular weights 425, 725, 2000, 3000, 4000 (Aldrich) and 1200 (Union Carbide) were dried at 50°C under reduced pressure (ca. 270 Pa) for a time necessary to achieve water contents of several tens of ppm: two days for PPD 425 up to three weeks for PPD 4000. The following characteristics of diols has been determined (Table 1): number-average molecular weights, M_n, by vapour-pressure osmometry, water content by coulometry and content of hydroxyl groups by the phenyl isocyanate method (reaction of polyols with excess of phenyl isocyanate, followed by reaction with dibutylamine (DBA) and potentiometric titration of unreacted DBA with HCl in isopropyl alcohol). The number-average functionality, f_n, was calculated from experimentally determined M_n and the hydroxyl content.

Table 1: Characteristics of poly(oxypropylene)diols

Type of diol	M_n	Hydroxyl content (%)	f_n	Water content (ppm)
PPD 425	425	8.03	2.00	16
PPD 725	730	4.52	1.95	61
PPD 1200	1230	2.64	1.94	83
PPD 2000	1900	1.71	1.92	51
PPD 3000	2490	1.27	1.86	69
PPD 4000	3260	0.98	1.89	59

The purity of diols was tested with an excess of phenyl isocyanate in bulk at 60°C for 72 h. The isocyanate consumption corresponded to the concentration of hydroxyls, i.e., diols did not contain an over-threshold concentration of substances acting as cyclotrimerization catalysts.

The remaining materials (phenyl isocyanate, 1,4-dioxane, dibutylamine, butyl-N-phenyl urethane and other standards) were prepared and treated as described elsewhere [7,8]. Cyclotrimerization catalyst, POLYCAT*41 (N,N′,N″-tris(3-dimethylaminopropyl)hexahydro-s-triazine; P41; Air Products), was used as received.

Reaction conditions

All reactions were performed in sealed glass ampoules in nitrogen atmosphere. A mixture of TDI and diol was poured into several ampoules, which were used for prepolymer testing or for network preparation. All prepolymers were synthetized at the ratio [NCO]/[OH] = 2/1. Networks were prepared from prepolymers by adding the catalyst (5 μl per g of prepolymer) and mixing it in the flow of nitrogen. Prepolymers were prepared at 60°C, and the networks at 80°C.

Determination of isocyanate groups

Unreacted isocyanate groups at various curing times were determined after reaction with an excess of DBA. In the case of prepolymer analysis, ca. 0.5 g of prepolymer was poured into conical flask, then 10 ml of 1,4-dioxane was added followed by DBA. Samples were titrated at least after one-hour mixing with 0.3 M HCl in isopropyl alcohol. Before titration, 5 ml of ethanol was added. The same procedure was used to check the isocyanate purity.

In the case of the networks a modified technique was used [9], in which the sample (ca. 0.5 g) was swollen in 15 ml of 1,4-dioxane containing an excess of DBA for the 48 h; then 7.5 ml of ethanol was added and the mixture was titrated with HCl until a constant value of pH in the point of equivalence was reached (i.e. up to 50 h). Due to adding of the POLYCAT*41 catalyst, which is a tertiary amine and reacts with HCl, the correction for the acid consumption by the catalyst was made in all cases.

Results and Discussion

During prepolymer preparation, urethane and urea groups can be formed under reaction conditions used (60°C, no catalyst). As the final consumption of isocyanate groups calculated after titration is close to the initial concentration of hydroxyl groups, there is no evidence that urea groups are formed. Therefore, the difference between the initial isocyanate concentration and its concentration after certain time is taken as hydroxyl conversion. From Figure 1, it is evident that the time needed for prepolymer

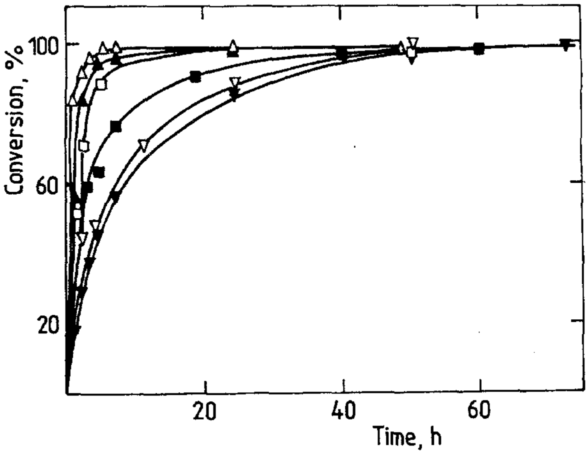

Figure 1: Time dependence of hydroxyl groups conversion during prepolymer preparation from 2,4-tolylene diisocyanate and poly(oxypropylene)diols: PPD 425 (△), PPD 725 (▲), PPD 1200 (□), PPD 2000 (■), PPD 3000 (▽) and PPD 4000 (▼) at reaction temperature 60°C

preparation is about 6 h for PPD 425, 24 h for PPD 725 and PPD 1200 and 48 h for PPD 2000, PPD 3000 and PPD 4000. Under these conditions all polyurethane prepolymers were prepared.

Poly(urethane-isocyanurate) networks were formed by adding the catalyst to prepolymers, the unreacted isocyanate groups were converted into the isocyanurate ones. The temperature 80°C was chosen for the preparation of networks for which the cyclotrimerization rate is still reasonable and other side reactions are minimized. Initial tests with the prepolymer from PPD 3000 and TDI showed that the optimum catalyst concentration was 5 μl of catalyst per g of prepolymer, which was used for preparation of all networks.

The course of cyclotrimerization was tested by determination of the unreacted isocyanate groups (Fig. 2). Curing time of 2 days for the prepolymer with PPD 425, 3 days with PPD 725, 4 days with PPD 1200, 5 days with PPD 2000 and PPD 3000 and of 6 days with PPD 4000 is sufficient; for a longer time the concentration of unreacted isocyanate remains constant < 0.2 meq/g, which corresponds to 2–7% of the initial concentration.

To test the reaction products during network formation from prepolymers, we have studied the model reaction of corresponding monofunctional components (phenyl isocyanate and butyl-N-phenyl urethane ($[NCO]/[NHCOO] = 1$)) with the same catalyst in 1,4-dioxane at 80°C. The time dependences of individual reaction products are shown in Figure 3. Urethane, isocyanurate (and urea) are dominant substances after sufficient reaction time (i.e. > 24 h). Allophanate and biuret are — after reaching a certain maximum concentration — gradually decomposed and their content after 48 h is negligible. The concentration of unreacted isocyanates decreases very slowly after 24 h.

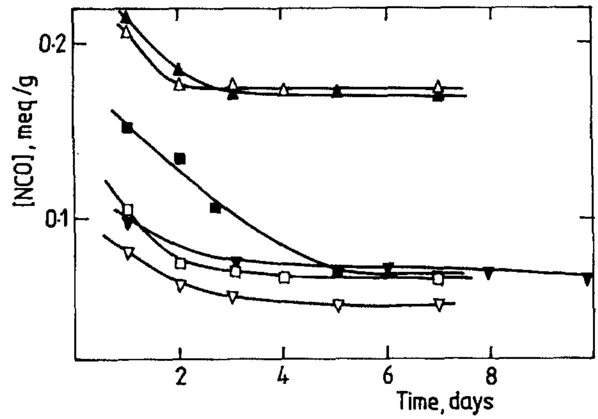

Figure 2: Time dependence of concentration of unreacted isocyanate groups in poly(urethane-isocyanurate) networks prepared from prepolymers of poly(oxypropylene)-diols: PPD 425 (△), PPD 725 (▲), PPD 1200 (□), PPD 2000 (■), PPD 3000 (▽) and PPD 4000 (▼); curing temperature 80°C

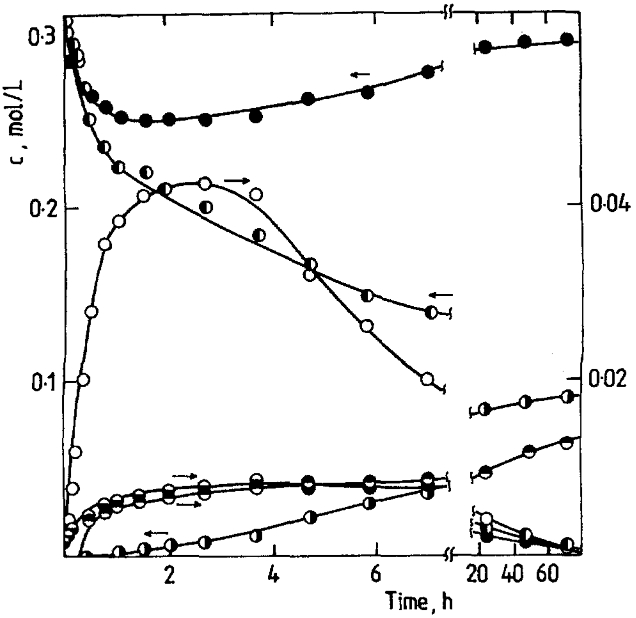

Figure 3: Time dependence of concentration of reaction products during cyclotrimerization of phenyl isocyanate (PhI) in the presence of butyl-N-phenyl urethane (BPU) and P41 catalyst in 1,4-dioxane at 80°C. Initial conditions: $(c_{\mathrm{PhI}})_o = 0.305$ mol.L^{-1}; $(c_{\mathrm{BPU}})_o = 0.295$ mol.L^{-1}, $c_{P41} = 5.1\times10^{-3}$ mol.L^{-1}; (◐) phenyl isocyanate, (◑) 1,3,5-triphenyl isocyanurate, (●) butyl-N-phenyl urethane, ◓)1,3-diphenylurea, (◒) 1,3,5-triphenylbiuret and (○) butyl-α,γ-diphenyl allophanate

These results were used for estimation of the concentrations of individual reaction groups in networks. The difference between the initial isocyanate concentration in the mixture of PPD and TDI and that in prepolymer after time t_1 (which is sufficient for full reaction of the hydroxyl groups) is taken as urethane concentration; urea concentration is considered to be zero. As allophanate (and biuret) concentrations can be neglected (t_2 is 48 h in the minimum), the difference between the initial concentration of the unreacted isocyanate groups in the prepolymer, $[\mathrm{NCO}]_{t_1}$, and that in network, $[\mathrm{NCO}]_{t_2}$, is considered to correspond to isocyanurate formation.

Initial and final concentrations of individual groups in prepolymers (at time t_1) and networks (at time t_2) are listed in Tables 2 and 3. Time t_1 is taken as the time sufficient for full reaction of hydroxyls in prepolymers, because the conversion of hydroxyl groups reaches 99–100%. Time t_2 is sufficient to reach a constant value of unreacted isocyanates during trimerization of prepolymers. The molar ratio of isocyanurate to urethane groups after the time t_2 is practically independent on the concentration of the catalyst P41.

Table 2: Concentrations of the reactive groups in prepolymers prepared from TDI and different PPD at 60°C

No.	Type of diol	$[NCO]_o$ meq/g	$[OH]_o$ meq/g	$[NCO]_o/[OH]_o$	Reaction time t_1, h	$[NCO]_{t_1}$ meq/g
1	PPD 425	5.18	2.57	2.02	6	2.64
2	PPD 725	3.75	1.81	2.07	24	1.94
3	PPD 1200	2.69	1.26	2.13	24	1.43
4	PPD 2000	1.72	0.85	2.02	48	0.88
5	PPD 3000	1.33	0.66	2.02	48	0.67
6	PPD 4000	1.07	0.51	2.12	48	0.56

Table 3: Concentrations of the isocyanate [NCO], urethane [U] and isocyanurate [I] groups in networks prepared at 80°C

Prepolymer No.	c_{P41}* mol%	Reaction time t_2, days	$[NCO]_{t_2}$ meq/g	[I] meq/g	[U] meq/g	[I]/[U]
1	0.47	2	0.17	0.82	2.54	0.32
2	0.63	3	0.17	0.59	1.81	0.33
3	0.84	4	0.07	0.45	1.26	0.36
4	1.40	5	0.07	0.27	0.84	0.33
5	1.80	5	0.05	0.21	0.66	0.32
6	2.15	6	0.07	0.16	0.51	0.31

* Relative to the concentration of isocyanate groups in prepolymers

The following conclusions can be made:

1. For synthesis of polyurethane prepolymers from 2,4-tolylene diisocyanate and α,ω-dihydroxypoly(oxypropylenes) at 60°C the optimum reaction time is 6 h for PPD 425, 24 h for PPD 725 and PPD 1200 and 48 h for PPD 2000, PPD 3000 and PPD 4000.
2. Poly(urethane-isocyanurate) networks can be easily prepared from prepolymers by adding a small amount of POLYCAT*41 catalyst (5 μl per g of prepolymer) at 80°C. Equilibrium isocyanate concentrations are reached for prepolymers from PPD 425 after 2 days, from PPD 725 after 3 days, from PPD 1200 after 4 days, from PPD 2000 and PPD 3000 after 5 days and from PPD 4000 after 6 days.
3. From the results of model reaction of monofunctional compounds (phenyl isocyanate and butyl-N-phenyl urethane) with P41 at 80°C in 1,4-dioxane and from isocyanate content in prepolymers and networks it is possible to calculate the content of urethane and isocyanurate groups in networks; (concentrations of allophanate and biuret groups are negligible).

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