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Comparative reactivities of hydroxylated polybutadienes with isocyanate in nitrobenzene

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Summary

The rates of reactions between two hydroxylated polybutadienes (R-45M and H-110) and 1,6-hexamethylene diisocyanate (HDI) have been studied in nitrobenzene solution in the temperature range from 30 to 60°C. An analytical method was used to follow the kinetics of the reactions. The second-order rate constants were calculated and it was concluded that the reactivities of the two -NCO groups in HDI are identical. The rate of the R-45M/HDI reaction is slightly higher and its activation energy is lower than that of the H-110/HDI reaction. The R-45M/HDI reaction is slower in nitrobenzene solution than in chlorobenzene solution.

Introduction

Polyurethanes can be formed by a variety of methods, although the most widely used production method is the reaction of di- or polyfunctional hydroxyl compounds with di- or polyfunctional isocyanates (1). The synthesis of hydroxyl-terminated polyhydrocarbons have opened the possibility toward the improvement of some chemical and physical properties of polyurethanes (2,3). The nonpolar main chain of hydroxyl-terminated polybutadienes(HTPB) provides polyurethane elastomers with superior hydrolytic stability (4). According to the synthesis condition, the HTPB varies in molecular weight, molecular weight distribution, functionality distribution and configurational structure (5).

Solvents play an important role in the rate of the uncatalyzed urethane reactions because they can reduce the concentration of self- associated hydroxyl groups (6). The phenomena of self- and heteroassociation of hydroxyl groups in solution through a hydrogen bond determine the kinetics of the reaction (7).

Although studies on kinetic of urethane reactions between alcohols and isocyanates are abundant, few kinetic studies about the reaction between HTPB and aliphatic diisocyanates are available at present. The aim of this work is to compare the reactivities of two hydroxylated polybutadienes (R-45M and H-110) (8) and 1,6 hexamethylene diisocyanate (HDI) in nitrobenzene solution with kinetic data obtained in a previous work (9).

Experimental

Materials

Hydroxyl-terminated polybutadienes were commercial products. (1) R-45M from ARCO Chemical Co., $\bar{M}_n$=2670, $\bar{M}_w/\bar{M}_n$=2.7, hydroxyl value = 0.77 meq/g, $\bar{F}_n$=2.06, (2) H-110 from PETROFLEX Indústria e Comércio S.A., $\bar{M}_n$=2440, $\bar{M}_w/\bar{M}_n$=2.5, hydroxyl value 0.84 meq/g, $\bar{F}_n$=2.05. The two polybutadienes were dried under reduced pressure and dry nitrogen in an 80°C oil bath for three hours. The molecular weights were measured in toluene, with a Wescan vapor pressure osmometer. Molecular weight distributions were measured by GPC in toluene at 25°C. The values of $\bar{F}_n$ (number average end functionality) were calculated from the product of $\bar{M}_n$ and the hydroxyl value. The hydroxyl values were determined by the acetic anhydride method. 1,6-Hexamethylene diisocyanate(HDI) from BAYER was refluxed over calcium hydride and distilled at 127°C/10 torr. Nitrobenzene PA-ACS from GRUPO QUÍMICA Industrial Ltda was dried over calcium chloride, filtered, refluxed with 4,4 -diphenyl methane diisocyanate(MDI) and distilled under reduced pressure. Di-n-butylamine from MERCK SCHUCHARDT was used as received.

Rate Measurements

Samples (in duplicate) were polymerized for different time intervals in individual reactors (100 ml), which were immersed in a constant temperature shaker bath. Each reactor contained 10 ml of a HTPB nitrobenzene solution (R-45M 30,0% w/w or H-110 27,9% w/w) and 5 ml of a 0.5 N HDI nitrobenzene solution. All solutions were prepared in order to obtain an NCO/OH ratio equal to 1.

At the end of each time interval, two samples were removed from the bath and quenched into an ice-water mixture. Then 50 ml of nitrobenzene and 2 ml of a 1:1 (volume ratio) of nitrobenzene and di-n-butylamine were added into each reactor. The solution was kept at room temperature for several hours to assure complete reaction of the unreacted isocyanate with the amine. The amine excess was measured by titration with 0.25 N hydrochloric acid. Before titration, 50 ml of ethanol and several drops of the indicator (1% 1:3 bromocresol green and methyl red in methanol) were added.

Results and Discussion

Reactions between HTPB(R-45M and H-110) and HDI were carried out at four temperatures (60,50,40 and 30°C). All reactions studied presented an apparent second-order rate law. Equivalent concentrations were used for both reactants, and the data were treated according to equation (1):

$$\frac{a}{a - x} = k\,a\,t + 1 \qquad (1)$$

where a = initial concentration for both reactants (eq/L),
a - x = residual concentration for both reactants (eq/L),
k = reaction rate constant (L/eq.hr), and t time (hr). Figures 1 and 2 show second-order plots corresponding to reactions of R-45M and H-110 respectively. As can be observed, the linear

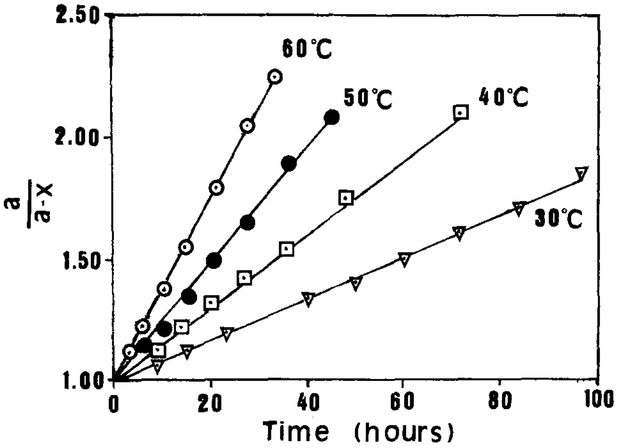


Figure 1
Second-order plots for reaction of HDI with HTPB (R-45M) in nitrobenzene at $[NCO]_o = [OH]_o$

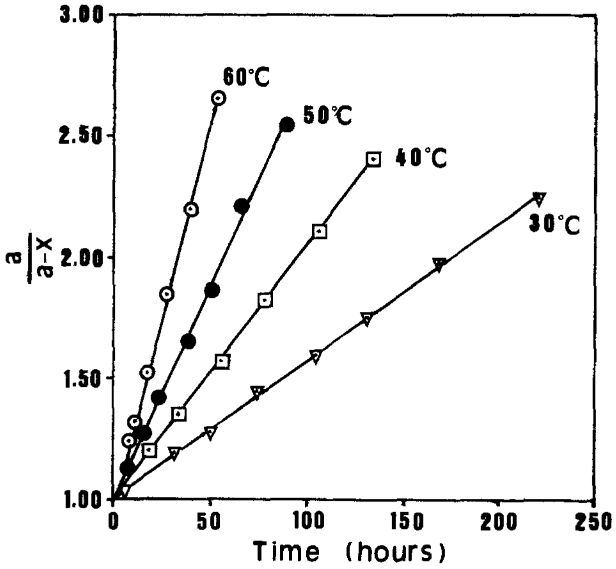


Figure 2
Second-order plots for reaction of HDI with HTPB (H-110) in nitrobenzene at $[NCO]_o = [OH]_o$

behavior of the plots, without breaks in the lines, is an indication that the two isocyanate groups have equivalent reactivities (10). In diisocyanates with isocyanate groups separated by aliphatic chains, the effect of one isocyanate or urethane group on the reactivity of the other one is less pronounced (1). Activation energies were calculated from the slope of the Arrhenius plot presented in Figure 3.

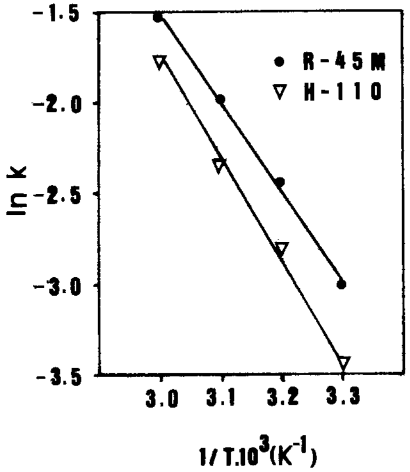
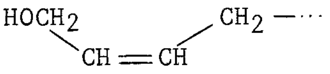
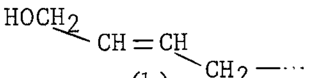


Figure 3
Arrhenius plot for reaction of HDI with HTPB (R-45M and H-110)

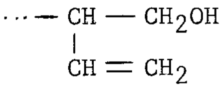
Table I shows values of the rate constant and activation energy. The R-45M/HDI reaction is slightly faster and its activation energy is lower than H-110/HDI reaction in nitrobenzene solution. As mentioned previously, the two HTPB have almost equivalent values of $\bar{F}_n$, although R-45M has a lower hydroxyl content. Additionally, it is known by NMR studies from literature (11) that HTPB obtained by free radical polymerization, using hydrogen peroxide as initiator and isopropyl alcohol as solvent, possesses at least 95% allylic primary hydroxyl groups and has usually the following types of primary hydroxyl functions (11,12):



(a)

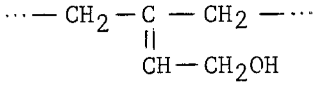


(b)



$\cdots-\underset{\substack{|\\ \mathrm{CH}=\mathrm{CH_2}}}{\mathrm{CH}}-\mathrm{CH_2OH}$

(c)



$\cdots-\mathrm{CH_2}-\underset{\substack{\|\\ \mathrm{CH}-\mathrm{CH_2OH}}}{\mathrm{C}}-\mathrm{CH_2}-\cdots$

(d)

The hydroxyl group in the structure"c"is the less reactive in reaction with isocyanates probably due to the steric hindrance of the vinyl group (12). The hydroxyl group in the structure "d" is the most reactive (12), and can be formed by chain transfer during the synthesis of HTPB, and contributes to the increase of the molecular weight distribution. The slightly higher value of $\bar{M}_w/\bar{M}_n$ suggests that R-45M contains more structure"d"than H-110. The microstructure of H-110 is not completely known yet. Thus, the difference of reactivities between the two HTPB seems to be related to the conformational effects of the polymeric chain due to branching and the distribution of the primary hydroxyl groups.

TABLE I

Reaction of 1,6-Hexamethylene Diisocyanate(HDI) and Hydroxylated Polybutadienes in Aromatic Solvents

Temperature (°C)	Nitrobenzene		Chlorobenzene*
	R-45M K(L/eq.hr)	H-110 k(L/eq.hr)	R-45M k(L/eq.hr)
30	0.05	0.03	0.13
40	0.09	0.06	0.22
50	0.14	0.10	0.34
60	0.22	0.18	0.53
E_a (kcal/mole)	9.81	11.81	9.40
[NCO] or [OH] (eq/L)	0.17	0.17	0.17

*Data taken from Ref. 9

The values of the rate constant listed in Table I show that R-45M/HDI reaction is slower in nitrobenzene than in chlorobenzene solution. Nitrobenzene having higher polarity and hydrogen bonding power than chlorobenzene, provides stronger interaction with hydroxyl groups reducing the concentration of associated alcohols and consequentely decreasing the rate of the reaction.

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Reference

1. J.H. Saunders and K.C. Frisch, Polyurethanes, Chemistry and Technology , Part I Chemistry, Wiley Interscience, New York, 1967.

2. J.P. Consaga and D.M. French, J. Appl. Polym. Sci., 15, 2941 (1971).

3. M. Ako and J.P. Kennedy, Polym. Bull., 19, 137 (1988).

4. B.B. Idage, S.P. Vernekar and N.D. Ghatge, J. Polym. Sci., Chem. Ed. 21, 385 (1983).

5. F.M.B. Coutinho, L.C. Rezende and J.R. Quijada, J. Polym. Sci., Chem. Ed. 24, 727 (1986).

6. A.E. Oberth and R.S. Bruenner, J. Phys. Chem. 72, 845 (1968).

7. P.A. Berlin, R.P. Tiger and S.G. Entelis, Kin. i Katal. 28, 1347 (1987).

8. W.D. Villar, Brazilian Patent No. 77.07.285 April 24, 1979.

9. M.C.G. Rocha, M.Sc. Thesis IMA, Universidade Federal do Rio de Janeiro, Brazil (1988).

10. F.M.B. Coutinho, L.C. Rezende and J.R. Quijada, J. Polym. Sci., Chem. Ed. 24, 3021 (1986).

11. K.C. Ramey, M.W. Hayes and A.G. Altenau, Macromolecules, 6, 795 (1983).

12. I. Descheres and Q.T. Pham, Makromol. Chem. 187, 1963 (1986).

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