

Exploration of the Difference of Reaction Rates for Polyester and Polyether Urethane Prepolymers with 3,3'-Dichloro-4,4'-Diaminodiphenylmethane

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SYNOPSIS

Polyester (PEPA) and polyether (PTMO) prepolymers with NCO end groups were synthesized. The chain extension reaction of these prepolymers with MOCA diamine was studied by FTIR spectrometry and found to be a second-order reaction. Data on chain extension reaction rate constants and activation energy showed that the chain extension reaction rate of the PEPA prepolymer with MOCA was faster than that of PTMO prepolymer with MOCA. Such a difference of chain extension reaction rate for PEPA and PTMO prepolymers with MOCA can be explained by hydrogen bonding interaction and miscibility between hard and soft segments in the cast polyurethane elastomer. The hydrogen bonding interactions of MOCA with PEPA prepolymer and PTMO prepolymer without chain extension reaction convincingly demonstrated the difference of chain extension reaction in the polyurethane-urea systems. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Cast polyurethane elastomer has been an important commercial product for a long time. It exhibits better mechanical strength, modulus, and thermal stability than thermoplastic polyurethane elastomer.

The term cast polyurethane elastomer is used here to refer to chemical systems that are cast by pouring techniques into molds for the purpose of fabricating products. Generally, the chemical systems consist of a prepolymer terminated with isocyanate and a small molecule diol or diamine. Moreover, it is well known that the choice of the suitable prepolymers and chain extenders (diol or diamine) is very important to gain good elastomer properties. In fact, the chain extender also acts as the crosslinking agent for cast urethane elastomer systems. Therefore, only a limited pour time is now available. The pour time is a very important

parameter for successfully producing good polyurethane elastomer. This limited pour time closely depends upon the prepolymer and the chain extender. It has been concluded that the reaction rate of the polyester prepolymer with a chain extender is faster than that of the polyether prepolymer. Also, the reaction of the diamine chain extension is faster. It is evident that polymer scientists are interested in investigating chain extension reaction kinetics.¹⁻⁴ However, little such research work is reported in the literature. In particular, why is the chain extension reaction of the polyether prepolymer with diamine slower than that of the polyester prepolymer? This should be answered clearly.

In the present work, 3,3'-dichloro-4,4'-diaminodiphenylmethane(MOCA) was chosen as the chain extender and the crosslinking agent. Commercial poly(ethylene-co-propylene adipate) and poly(tetramethylene oxide) with toluene diisocyanate (2,4-TDI) formed prepolymers, respectively. The kinetics of the chain extension reaction for the mentioned systems were studied by infrared spectroscopy. Finally, the differences of the chain

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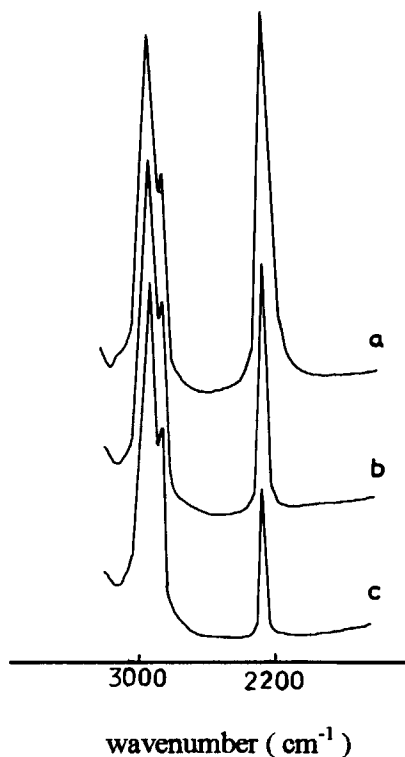


Figure 1 The change of NCO absorption band with time in the chain extension reaction of PEPA prepolymer with MOCA at 336 K. (a) 0 s; (b) 1237 s; (c) 3142 s.

extension reactions for polyester and polyether prepolymers with MOCA are discussed.

EXPERIMENTAL

Materials

The poly(ethylene-co-propylene adipate) (PEPA) samples with a number average molecular weight of $M_n = 2,000$ and terminated with hydroxyl groups were made in the factory of synthetic leather in Yan Tai.

The poly(tetramethylene oxide) diol (PTMO) samples with a number average molecular weight of $M_n = 2,000$ were supplied by Polyscience Inc., Warrington, PA.

The toluene diisocyanate (2,4-TDI) was produced by the Shanghai Chemical Agent Factory. It was repurified by distilling before use in preparation of the prepolymers.

The polyester (PEPA) and polyether (PTMO) first were degassed and dried under high vacuum (0.1 mmHg) at 105°C for 3 h. Then the temperature was decreased to 70°C, the 2,4-TDI was added into the reaction flask at a molar ratio NCO/OH = 2 :

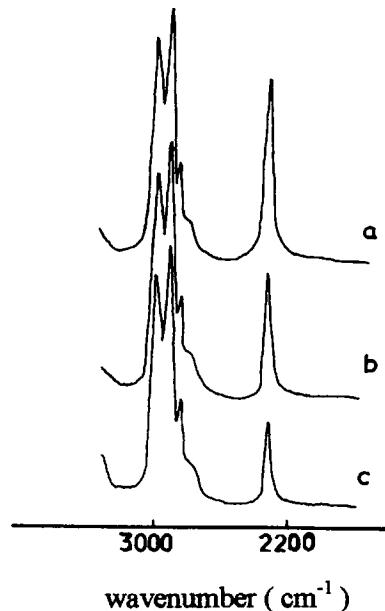


Figure 2 The change of NCO absorption band with time in the chain extension reaction of PTMO prepolymer with MOCA at 355 K. (a) 84 s; (b) 1020 s; (c) 2070 s.

1. The reaction was conducted smoothly for 3 h. The prepolymers so synthesized were kept in a desiccator.

The 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA), used as a chain extender, was produced by the factory of Qian Jin Chemistry Industry in Su Zhiu. It was recrystallized before use in the I-R spectroscopy experiments.

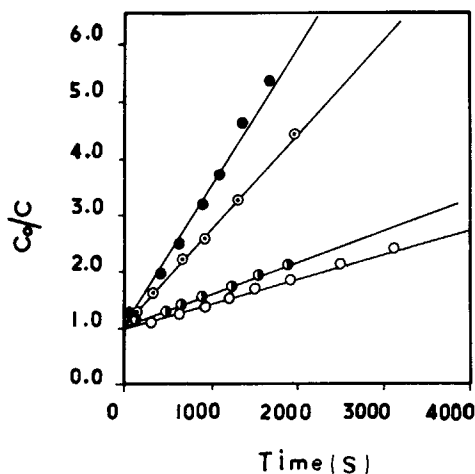


Figure 3 The change of NCO concentrations with chain extension reaction at four different temperatures for PEPA prepolymer and MOCA system. (○) 336 K; (●) 342 K; (○) 369 K; (●) 377 K.

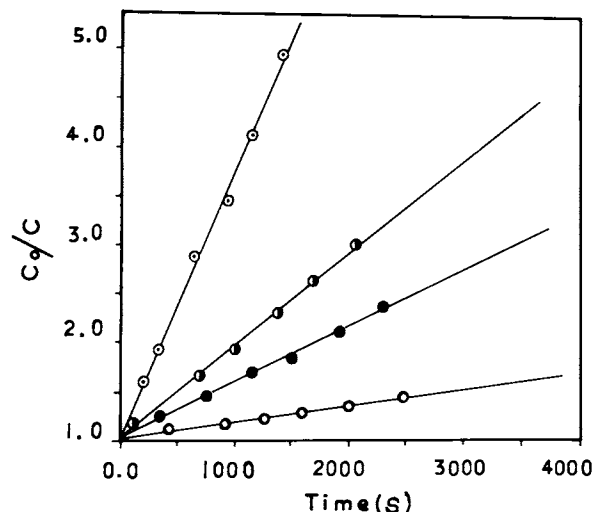


Figure 4 The change of NCO concentrations with chain extension reaction at four different temperature for PTMO prepolymer and MOCA system. (○) 331 K; (●) 344 K; (◐) 355 K; (⊙) 373 K.

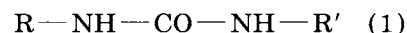
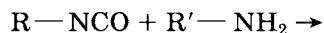
Infrared Measurements

The chain extension reaction of the different prepolymers with end isocyanate groups and MOCA was monitored by a Nicolet 170SX Fourier Transform Infrared Spectrometer. The NCO stretching vibration band at 2274 cm^{-1} is a sensitive band and used to trace the chain extension reaction, as shown in Figures 1 and 2. At the same time, the C—H stretching vibration bands at 2951 cm^{-1} and 2869 cm^{-1} for PEPA (2943 cm^{-1} and 2853 cm^{-1} for PTMO) do not change during reaction and were chosen as internal reference standards. Spectra of the kinetic runs were taken with a software-controlled data collection routine. All spectra were run at the resolution of 2 cm^{-1} and were signal averaged for 32 scans. The temperature of the sample oven was controlled by a thermoregulator.

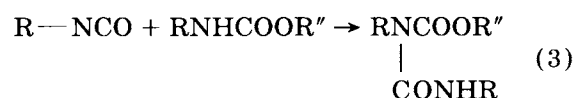
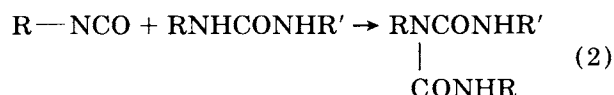
The samples for study of the chain extension reaction by infrared measurements were prepared by following procedure. The prepolymers and MOCA were dissolved in the dry solvent CH_2Cl_2 at an equimolar ratio NCO/NH_2 . The mixture solution was first dropped on a NaCl plate, then transferred into a desiccator with a pump: the solvent CH_2Cl_2 was removed in a vacuum at a room temperature of 20°C . The second NaCl plate covered the dried samples and, after fixing, it was again put into the oven at a chosen reaction temperature to measure the change of the band at 2274 cm^{-1} with time.

RESULTS AND DISCUSSION

It is well known that the reaction of isocyanate with diamine can be described by the following formula:



At the same time, secondary reactions may lead to the formation of biuret and allophanate:



Generally, these secondary reactions occur at higher temperatures. The possibility of forming allophanate is smaller, in particular. The formation of biuret and allophanate means that branching and crosslinking occur in the system, which are important considerations for cast polyurethane elastomer. However, the investigation of the kinetics of the polyurethane system usually needs to be simplified, as shown in earlier work.⁵ Therefore, an equal molar ratio NCO/NH_2 in the cast polyurethane system was used: under the equal molar ratio NCO/NH_2 , i.e., at 100% of the theoretical MOCA level, the degree of

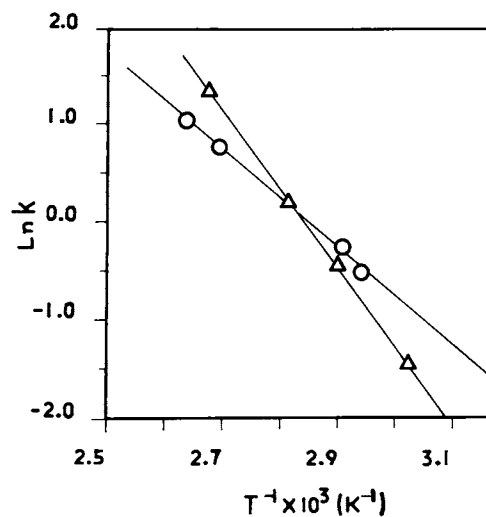


Figure 5 The plot of constant of the chain extension reaction rate against temperature for (○) PEPA prepolymer with MOCA, (△) PTMO prepolymer with MOCA systems.

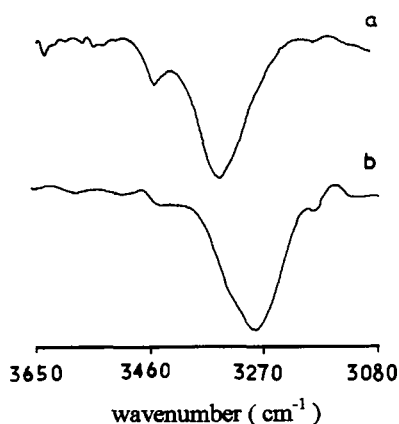
Table I The Kinetic Data of These Chain Extension Reactions

Systems	Temperature (<i>T</i>) and Rate Constant (<i>k</i>)					Activation Energy (kJ/mol)
	<i>T</i> (K)	<i>k</i> (g/mol·s)	<i>T</i> (K)	<i>k</i> (g/mol·s)	<i>T</i> (K)	
PEPA prepolymer and MOCA	336	0.566	342	0.736	369	42.7
	377	3.08				
PTMO prepolymer and MOCA	331	0.230	344	0.678	355	66.8
	373	3.71				

branching and crosslinking is at a minimum. (In industry, to obtain an acceptable level of general properties, a MOCA concentration of 90–95% of the theoretical is recommended.) It can be concluded that in the system of prepolymers and MOCA with equal molar ratio NCO/NH₂ at a suitable temperature, the chain extension reaction should predominate. In such a case, the reaction rate formula is simple:

$$d[\text{urea}]/dt = k[\text{NCO}][\text{NH}_2] \quad (4)$$

For the systems of polyester (PEPA) and polyether (PTMO) with MOCA, the NCO stretching vibration band is an isolated and sharp band, ideal for observation of kinetics. First, the chain extension reaction of PEPA and MOCA was observed. It has been proposed that the chain extension reaction is a second-order reaction. Therefore, the NCO concentration ratio (C_0/C) was plotted against reaction time, and, indeed, a straight line was obtained. At four different temperatures the changes of the NCO concentration with reaction time were measured. C_0 is the NCO concentration before beginning reaction, and is 7.65×10^{-4} mol/g. The concentrations C were

**Figure 6** NH bands of PEPA (a) and PTMO (b) prepolymer.

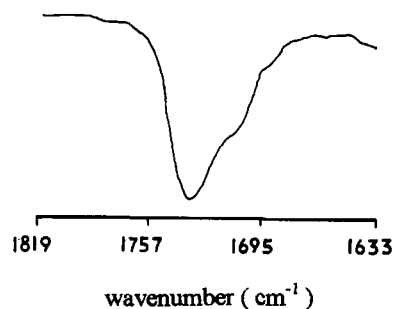
determined by using the corrected band area at 2274 cm^{-1} and original concentration C_0 . From the slopes of four straight lines in Figure 3 the constants of the chain extension reaction rate at different temperatures were obtained. The constants of the reaction rate were plotted against the temperatures by the Arrhenius formula, as shown in Figure 5, and the straight line obtained can give the activation energy for the PEPA-prepolymer-MOCA system.

For the PTMO prepolymer-MOCA system the process just mentioned can be repeated. From corresponding plots of C_0/C against reaction time as shown in Figure 4, the constants of the chain extension reaction rate at different temperatures were obtained. The activation energy for the PTMO prepolymer-MOCA system was obtained from Figure 5 in the same way.

The data for reaction rate constants and activation energy for PEPA prepolymer-MOCA and PTMO prepolymer-MOCA systems are listed in Table I.

From these results, it can be seen that the reaction of the PEPA prepolymer-MOCA system is faster and the activation energy of the PTMO prepolymer-MOCA system is larger. How can we understand such a difference in reaction rate and activation energy for polyester and polyether systems?

In the systems of PEPA prepolymer-MOCA and PTMO prepolymer-MOCA there are the same reaction groups—NCO and—NH₂, moreover, the soft

**Figure 7** Carbonyl bands of PTMO prepolymer.

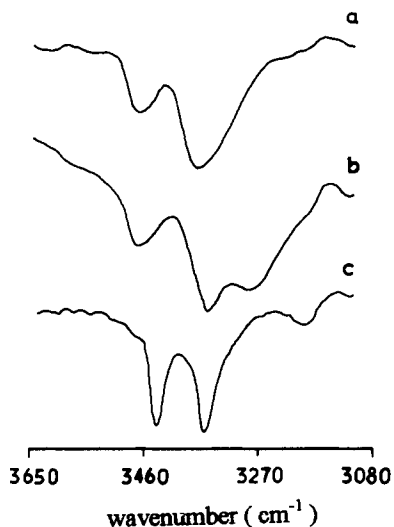


Figure 8 NH bands of mixtures of PEPA (a) prepolymer, PTMO (b) prepolymer with MOCA, and pure MOCA (c).

segments do not take part in the chain extension reaction. How can the polyester and polyether segments influence the reaction rate of the systems? It is a reasonable deduction that the hydrogen bonding between hard segments and soft segments in the above-mentioned cast systems should play an important role. In fact, Cooper et al.⁶ have systematically studied the hydrogen bonds in polyurethane by IR spectroscopy and shown that at room temperature, about 80% of the NH groups in the polyether-based and polyester-based polyurethanes were estimated to form hydrogen bonds, and for the PTMO-based polyurethanes, about 65% of carbonyl groups participated in hydrogen bond formation with the NH groups while the ether oxygen presumably accounts for the rest of the NH association. Moreover, the hard-soft segment hydrogen bond was found to be weaker than the interurethane bond and was found to dissociate first when the polymers were heated from room temperature. Mao Xu et al.⁸ also came to a similar conclusion by FTIR spectroscopy.

At the same time, DSC data⁶ indicated that the glass transition temperature T_g changes with the content of hard segments in PTMA-based polyurethane, but not so in PTMO-based polyurethane. In our laboratory, similar experimental results⁷ were observed. Such results suggested a better phase separation in the PTMO-based polyurethanes and considerable hard-soft segment phase intermixing in polyester-based polyurethanes.

In the present work, the systems consist of two components: NCO-terminated PEPA or PTMO prepolymers and MOCA chain extender. First, the

spectra of PEPA and PTMO prepolymers were measured and the NH stretching vibration bands are shown in Figure 6. It is evident that the bonded NH stretching band shifts to a lower wavenumber (3288 cm^{-1}) for the PTMO prepolymer. Christenson et al.⁹ proved that the splitting of the bonded NH band is related to different acceptors with which the NH groups are hydrogen bonded, and the bands at 3325 and 3260 cm^{-1} were assigned to NH groups bonded with carbonyl (in hard segments) and ether oxygens (in polypropylene-oxide soft segments), respectively.

In the PTMO prepolymer, the NH band at 3288 cm^{-1} should be assigned to the NH group bonds mainly with ether oxygens. The carbonyl stretching band of the PTMO prepolymer is shown in Figure 7. It is evident that the unbonded carbonyl band at 1735 cm^{-1} is stronger and the bonded carbonyl band, as a shoulder at 1711 cm^{-1} , is weaker. Such experimental results also confirmed that the content of NH groups bonded with carbonyl groups in hard segments is less. This can be understood for the PTMO prepolymer in which the urethane groups are far fewer than the ether oxygens.

The spectra of the chain extender MOCA and the mixtures of MOCA with an NCO terminated PEPA prepolymer or a PTMO prepolymer are shown in Figure 8. The corresponding wavenumbers of NH bands are listed in Table II.

The NH band of MOCA is split into two separated bands at 3442 cm^{-1} and 3362 cm^{-1} . The former is the unbonded NH band and the latter is the bonded NH band. For a mixture of PEPA prepolymer and MOCA, the NH bands shift from 3346 cm^{-1} and 3452 cm^{-1} (for pure PEPA prepolymer) to 3369 and 3464 cm^{-1} . This is the result of adding MOCA. The hydrogen bond of pure MOCA, and the hydrogen bond of MOCA with carbonyl in the PEPA prepolymer, are weaker. For a mixture of the PTMO prepolymer and MOCA, the NH bands shift to 3291 ,

Table II The Wavenumber of NH Stretching Vibration Bands for MOCA, PEPA, or PTMO Prepolymer, and Their Mixtures

Samples	NH Stretching Vibration Bands (cm^{-1})	
MOCA	3362	3442
PEPA prepolymer	3346	3452
PEPA prepolymer with MOCA	3369	3464
PTMO prepolymer	3288	
PTMO prepolymer with MOCA	3291	3352 3468

3352, and 3468 cm^{-1} . The band at 3291 cm^{-1} should be assigned to bonded NH groups in the PTMO prepolymer, the band at 3353 cm^{-1} is the band of bonded NH group in the MOCA, and the band at 3468 cm^{-1} belongs to the unbonded NH group in the MOCA. It is very interesting that the wavenumber of the bonded NH band in the MOCA, for the PTMO prepolymer mixture with MOCA, is lower than that in pure MOCA, while the situation is reversed in the PEPA prepolymer mixture with MOCA. This means that the NH hydrogen bond of MOCA with ether oxygen in the PTMO prepolymer is stronger than that in pure MOCA, but the NH hydrogen bond of MOCA with carbonyl in the PEPA prepolymer is weaker than that in pure MOCA.

For the present prepolymer-MOCA systems, the chain extension reaction proceeds at temperatures higher than 65°C. At such temperatures, as the reaction proceeds, the mixing of soft and hard segments of the PTMO prepolymer-MOCA system in particular becomes worse and worse. The hydrogen bonds of NH groups in urethane with ether oxygen dissociate continuously.⁴

All these trends are unfavorable for contact of NH_2 groups in the MOCA with NCO end groups in the PTMO prepolymer. Therefore, the chain exten-

sion reaction in the mixture of the PTMO prepolymer with MOCA should be slower in a certain range of the reaction temperature.

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