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Thermal Stability of Isocyanate-Based Polymers. 2. Kinetics of the Thermal Dissociation of Model Urethane, Oxazolidone, and Isocyanurate Block Copolymers

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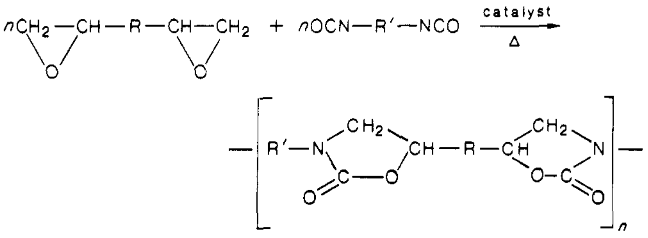
ABSTRACT: The thermostability of model block copolymers (urethanes, oxazolidones, and isocyanurates) was studied by dynamic and isothermal thermogravimetric analysis. The kinetic data obtained by isothermal TGA showed that the thermostability of the block copolymers (with similar block structure) increased in the following order: urethanes < oxazolidones < isocyanurates. The comparison of the kinetic parameters (rate constants, activation energies) obtained by cleavage of the urethane groups, oxazolidone, and isocyanurate rings determined by IR spectroscopy on the model compounds showed that in the case of urethane block copolymers the degradation proceeds through cleavage of the urethane groups. In the case of oxazolidone block copolymers it was established that the degradation probably proceeds by the parallel scission of the oxazolidone rings and aryl–isopropylidene bonds. The degradation of isocyanurates through cleavage of isocyanurate rings was complimented with a cross-linking char-forming reaction. The thermostability of urethane groups and oxazolidone and isocyanurate rings is affected by the neighboring substituent.

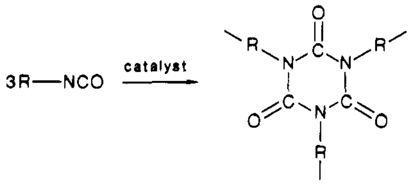
Introduction

Urethane block copolymers have excellent mechanical properties and therefore have found many applications in industry as elastomers, cellular materials, coatings, and adhesives. However, at high-temperature applications, these block copolymers have a limited use due to the relatively low thermostability of the urethane groups.

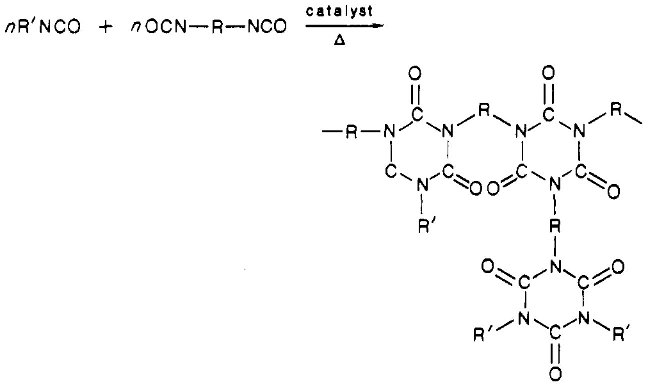
The thermal stability of these block copolymers could be increased by the replacement of the urethane groups by more heat resistant heterocyclic groups in the polymer chain. Such thermostable groups which can be formed from isocyanates are oxazolidones and isocyanurates (*s*-triazine-2,4,6(1*H*,3*H*,5*H*)-trione). The polyoxazolidones can be prepared by reaction of diepoxides with diisocyanates (or NCO-terminated prepolymers) according to the following equation:[1-12]



Polyisocyanurates could be synthesized by cyclotrimerization of difunctional isocyanates or by cocyclotrimerization of difunctional isocyanates with monofunctional isocyanates. In the first case, the resulting polymer will contain isocyanurate rings as cross-links:



In the second case, the structure of the polymers (branching, cross-link density) will depend on the molecular ratio of monoisocyanate to diisocyanate. At the equimolar ratio of isocyanates, a soluble, branched cocyclotrimer can be prepared:



In our previous paper,[13] the kinetics of the thermal dissociation of urethane, oxazolidone, and isocyanurate groups were measured on low molecular weight model compounds. It was determined that the thermal stability of the above-mentioned groups decreased in the following order: isocyanurates > oxazolidones > urethanes.

In this paper the thermal stability of the model block copolymers containing urethane, oxazolidone, and isocyanurate groups with similar polymer chains will be reported. The results obtained on these block copolymers by isothermal and dynamic thermogravimetric analysis will be discussed and compared with the kinetic data of the cleavage of urethane, oxazolidone, and isocyanurate groups, published previously.

Using this comparative methodology it was possible to determine the "weak groups" in polymers, where the degradation by the random chain scission took place.

Experimental Section

Preparation of Model Polymers. All the reactions for the preparation of the model polymers were carried out in similar manner to those for the preparation of the model compounds.[13] The 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane that was used for the preparation of the model urethanes was prepared from 2,2-bis(4-hydroxyphenyl)propane and 2-chloroethanol, according to ref 14.

Preparation of Model Polyurethanes. To a 300-mL three-necked flask equipped with a nitrogen inlet, stirrer, reflux condenser, and thermometer were added 0.1 mol of 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane, 0.1 mol of diphenylmethane-4,4′-diisocyanate (MDI), 50 mL of benzene, and 0.02%

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w/w stannous octoate (T-9). The flask was immersed in a constant-temperature oil bath kept at 70 °C. The progress of the reaction was determined by the NCO group analysis. After 30 min of reaction, the NCO percentage dropped to 1.98% (45.2% conversion). At this point the polymer began to precipitate. Fifty milliliters of dimethyl formamide (DMF) were added and the reaction was continued for a total of 5 h. The polymer (PUR-I) was precipitated in 500 mL of ethanol. Then it was filtered, recrystallized from DMF, and dried in a vacuum oven at 60 °C overnight. The product had an inherent viscosity η_{inh} = 0.44 in DMF; IR 1725 cm^{-1} (ν(C=O)). Anal. Calcd for $C_{27}H_{36}O_6N_2$: C, 72.1; H, 6.0; N, 4.9. Found: C, 72.2; H, 6.0; N, 4.8.

Polyurethane (PUR-II) obtained from 2,2-bis[4-(β-hydroxyethoxy)phenyl]propane and 1,6-hexamethylene diisocyanate was prepared in the same manner as described above.

Preparation of Model Polyoxazolidones. To a 300-mL three-necked flask, equipped with a nitrogen inlet, stirrer, reflux condenser, and thermometer, were added 0.5 mol of 2,2-bis[*p*-(2,3-epoxypropoxy)phenyl]propane (DER-332), 0.5 mol of 1,6-hexamethylene diisocyanate, 150 mL of DMF, and 0.5% w/w (based on reactants) of diethyl zinc. The flask was immersed in a constant-temperature oil bath kept at 150 °C. The progress of the reaction was determined by NCO group analysis. After 12 h the reaction was stopped and the polymer (POX-II) precipitated in 500 mL of ethanol. Then it was filtered and dried in a vacuum oven at 60 °C overnight. The product had an inherent viscosity η_{inh} = 0.31 in DMF, IR 1750 cm^{-1} (ν(C=O)). Anal. Calcd for $C_{28}H_{35}O_6N_2$: C, 67.7; H, 7.3; N, 5.6. Found: C, 67.4; H, 7.2; N, 5.5.

Polyoxazolidone (POX-I) obtained from DER-332 and MDI was similarly prepared.

Preparation of Model Polyisocyanurates. To a 300-mL three-necked flask equipped with a nitrogen inlet, stirrer, reflux condenser, and thermometer were added 0.1 mol of 1,6-hexamethylene diisocyanate, 0.1 mol of butyl isocyanate, 200 mL of DMF, and 1% w/w (based on reactants) sodium ethoxide. The flask was immersed in a constant-temperature oil bath which was kept at 70 °C. The progress of the reaction was determined by NCO group analysis. After 10 h the reaction was stopped and the polymer (PTR-II) precipitated in 500 mL of ethanol. Then it was filtered and dried in a vacuum oven at 70 °C overnight. The product was soluble in DMF and had an inherent viscosity η_{inh} = 0.31 in DMF; IR 1690 cm^{-1} (ν(C=O)). Anal. Calcd for $C_{13}H_{21}O_3N_3$: C, 58.4; H, 7.9; N, 15.7. Found: C, 58.2; H, 7.9; N, 15.9.

Polyisocyanurate (PTR-I) obtained from MDI and phenyl isocyanate was similarly prepared by using *N,N′,N″*-tris[(dimethylamino)propyl]-*s*-hexahydrotriazine as catalyst.

Thermal Decomposition of Model Polymers. The thermal degradation of model polymers was studied by means of thermogravimetric analysis. The thermogravimetric studies were conducted by using a Du Pont 900 thermobalance. The dynamic TGA curves were obtained at a linear heating rate of 15 °C min^{-1}. The accuracy of the temperature reading was ±1 °C. The sample weight was 10–12 mg. The isothermal TGA measurements were obtained at different temperatures at a time axis scale of 10 min/in. and 20 min/in. All measurements were conducted under N_2.

Analytical Methods. The determination of the percent isocyanate group was carried out according to the method described in ref 15. The percent epoxide group was measured according to the method of Dijkstra and Dahmen.[16] The elemental analyses were carried out by Midwest-Microlab, Ltd., Indianapolis, IN 46250.

Results and Discussion

Polycocyclotrimers of Isocyanates—Reaction, Kinetics, and Preparation. The model polyisocyanurates were synthesized by polycocyclotrimerization of monofunctional and difunctional comonomers. Previous investigators[1] on polycocyclotrimerizations had suggested that the relative rates of trimerization of the monofunctional and difunctional comonomers were very critical in the formation of un-cross-linked copolymers. Consequently the rates of trimerization of the following monofunctional and difunctional isocyanate systems were investigated:

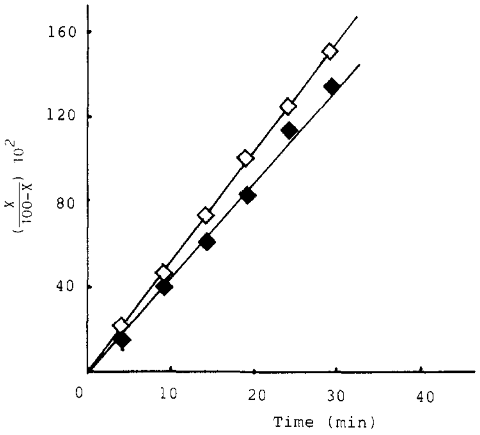


Figure 1. Kinetics of trimerization of phenyl isocyanate (◇) and diphenylmethane-4,4′-diisocyanate (◆); X = % NCO conversion. T = 70 °C, 0.1 mol of isocyanate in 200 mL of DMF and 1% w/w (based on isocyanate) *N,N′,N″*-tris[(dimethylamino)propyl]-*s*-hexahydrotriazine as catalyst.

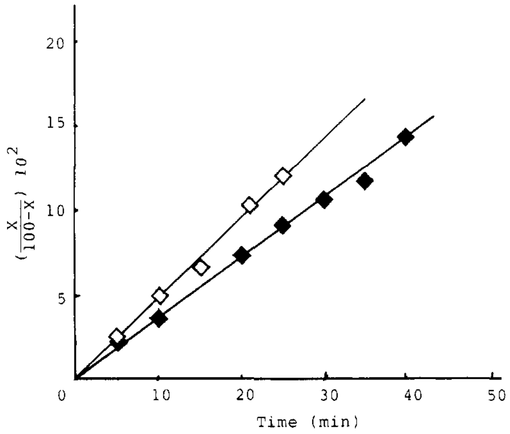


Figure 2. Kinetics of trimerization of butyl isocyanate (◇) and 1,6-hexamethylene diisocyanate (◆). T = 70 °C, 0.1 mol of isocyanate in 200 mL of DMF and 1% w/w (based on isocyanate) sodium ethoxide catalyst.

system A $OCNC_6H_4CH_2C_6H_4NCO$, C_6H_5NCO

system B $OCN-(CH_2)_6-NCO$, $CH_3CH_2CH_2CH_2NCO$

system C $OCNC_6H_{10}CH_2C_6H_{10}NCO$, $C_6H_{11}NCO$

The kinetics of trimerization of the above systems were studied by measuring the change in the concentration of the NCO group at regular time intervals. The disappearance of the NCO groups correlated with the second reaction order. The kinetic data are summarized in Figures 1–3. These data show that the trimerization rates of the difunctional and monofunctional isocyanates of systems A and B were close enough to permit the formation of un-cross-linked copolymers. Therefore, model polyisocyanurates (PTR-I and PTR-II) were synthesized employing reaction conditions that were used in the kinetic study. In both reactions the NCO conversion reached 100%. Both polymers were soluble in DMF. The formation of polycocyclotrimers was confirmed by the IR spectra of PTR-I and PTR-II and elemental analysis.

The kinetic data for system C (Figure 3) showed that the rate of trimerization of the difunctional monomer was quite different from that of the monofunctional monomer. As was expected, an attempt to prepare a copolymer from system C led to the formation of a cross-linked product. This indicates that the two comonomers trimerized to a

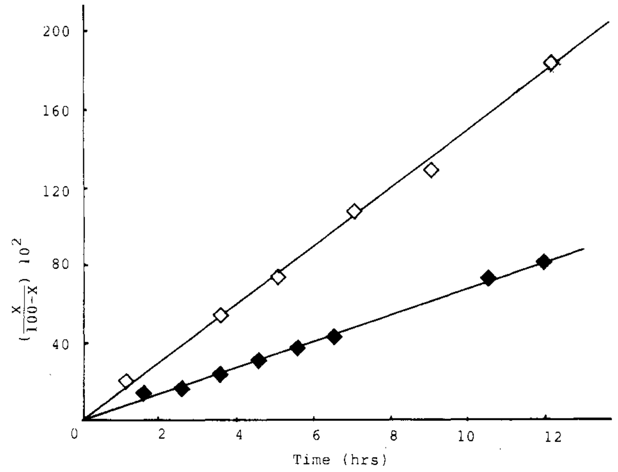


Figure 3. Kinetics of trimerization of cyclohexyl isocyanate (◇) and dicyclohexylmethane-4,4′-diisocyanate (◆). $T = 70$ °C, 0.1 mol of isocyanate in 200 mL of DMF and 1% w/w (based on isocyanate) sodium ethoxide catalyst.

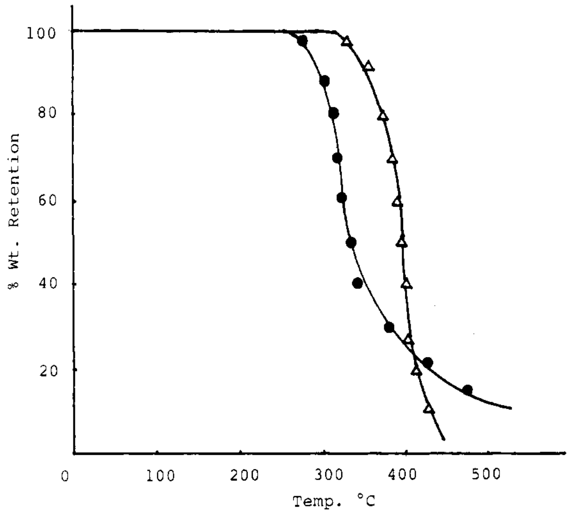


Figure 4. Dynamic thermogravimetric analysis of model polyurethanes: (●) PUR-I; (△) PUR-II.

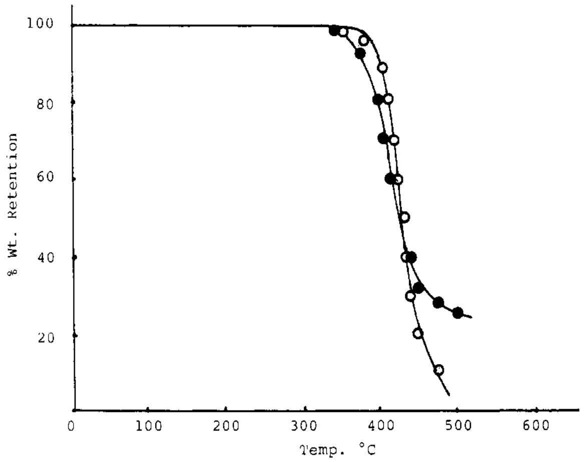


Figure 5. Dynamic thermogravimetric analysis of model polyoxazolidones: (○) POX-II; (●) POX-I.

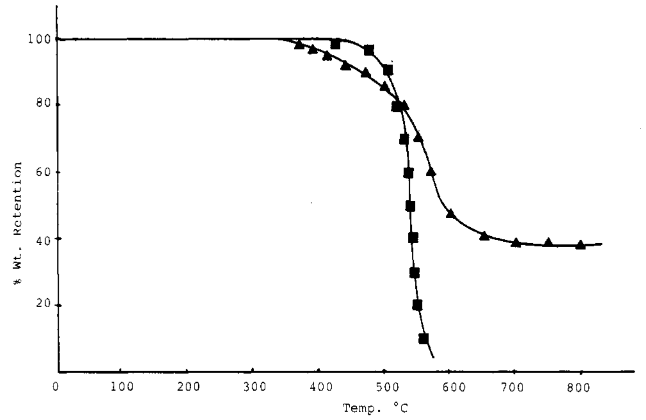


Figure 6. Dynamic thermogravimetric analysis of model polyisocyanurates: (■) PTR-II; (▲) PTR-I.

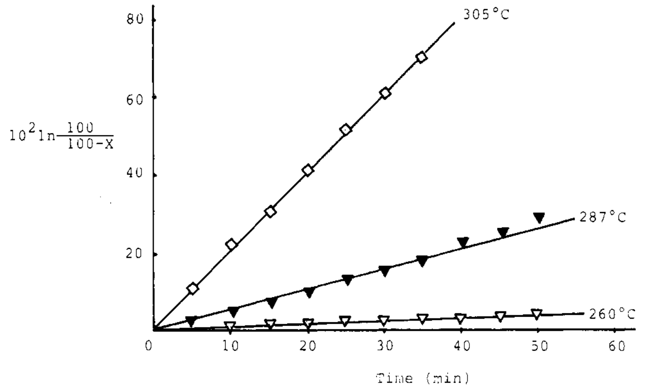


Figure 7. Kinetics of thermal degradation of model polyurethane (PUR-I).

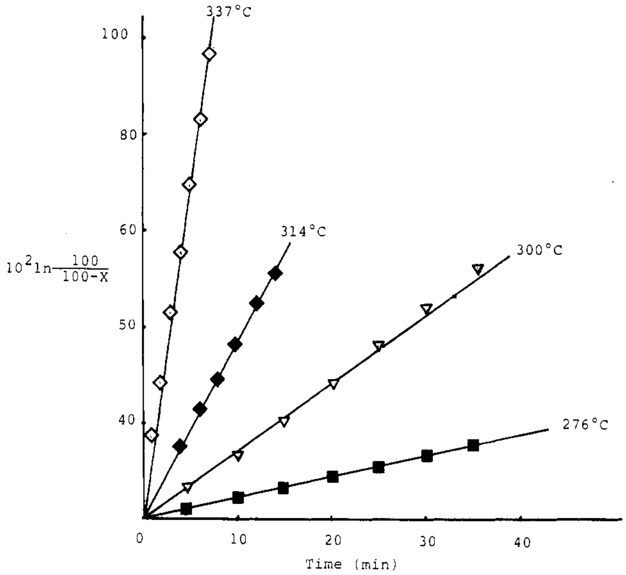


Figure 8. Kinetics of thermal decomposition of model polyurethane (PUR-II).

certain degree independently.

Thermostability of Model Block Copolymers. The structure of the model polymers whose thermal stability was investigated is shown in Table I. The thermal degradation of the model polymers was investigated by means of dynamic and isothermal TGA. Dynamic TGA (Figures 4–6) showed that the decomposition of model polyurethanes occurred in the temperature range 260–360 °C and model polyoxazolidones decomposed in the range of 330–360 °C, whereas model polyisocyanurates decomposed at 380–420 °C.

The kinetic measurements carried out by means of isothermal TGA correlated with the following equation:

$$-\frac{\mathrm{d}(w)}{\mathrm{d}t} = k[w] = [w]Ae^{-E/(RT)}$$

where w = weight of nondegraded sample, indicating that the rate of evaporation of the volatile degradation products

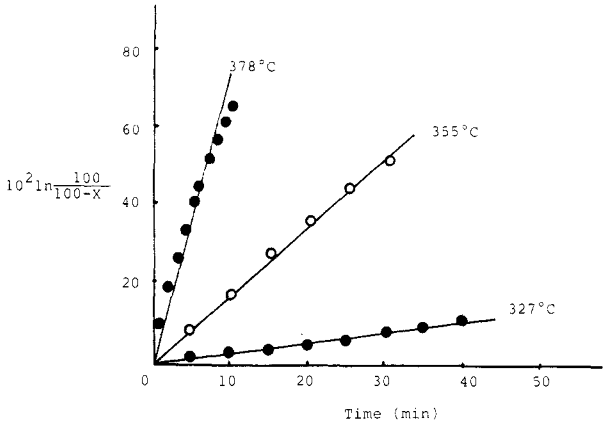


Figure 9. Kinetics of thermal degradation of model polyoxazolidone (POX-I).

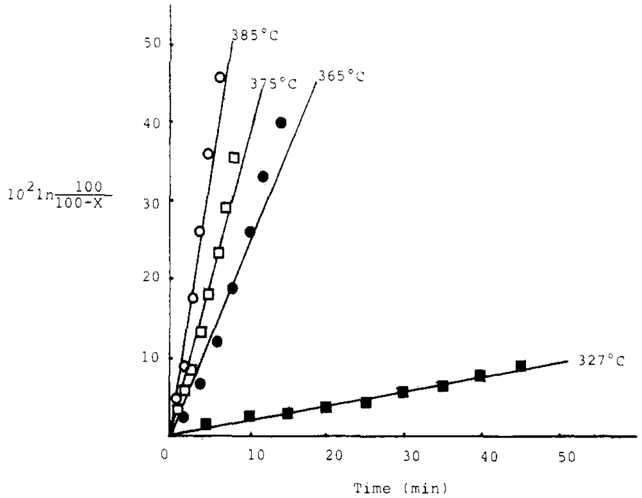


Figure 10. Kinetics of the thermal decomposition of model polyoxazolidone (POX-II).

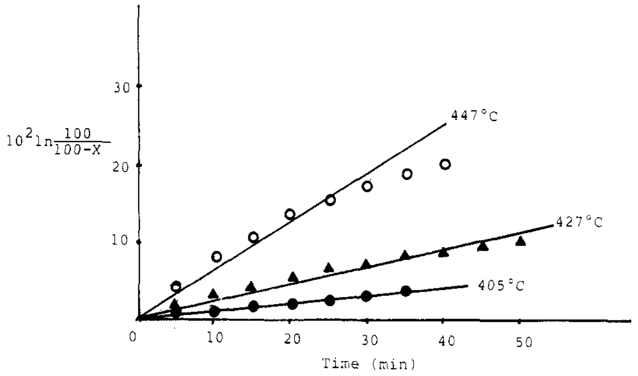


Figure 11. Kinetics of the thermal decomposition of model polyisocyanurate (PTR-I).

was fast (under these experimental conditions) and that the rate-determining step was the cleavage of the polymer chain.[18]

The results of the kinetic measurements are in Figures 7–13. The rate constants, activation energies, and frequency factors are summarized in Table II.

Comparison of the Kinetic Data of Decomposition of Model Polymers and Model Compounds. In our previous paper,[13] the kinetic data for the selective group cleavage (urethane groups, oxazolidone, and isocyanurate rings) measured on model compounds by the IR technique were presented. Those results will be compared with the kinetic data obtained on the model polymers by means of isothermal TG analysis.

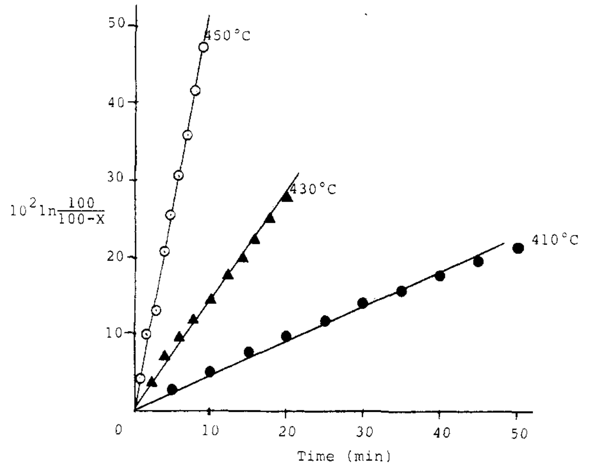


Figure 12. Kinetics of the thermal decomposition of model polyisocyanurate (PTR-II).

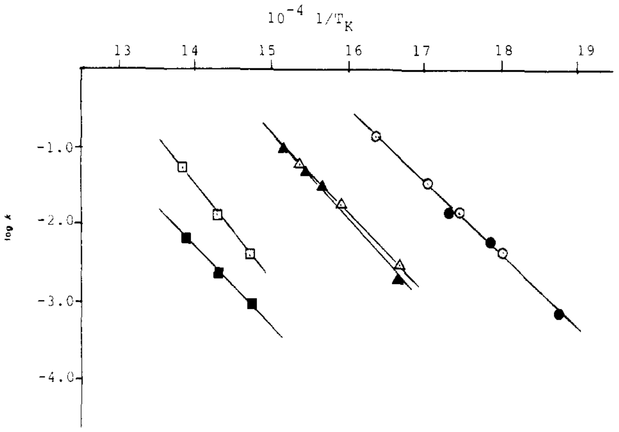


Figure 13. Arrhenius plots for model polymers: (○) PUR-II; (●) PUR-I; (▲) POX-II; (△) POX-I; (□) PTR-II; (■) PTR-I.

It is known[19,20] that block copolymers undergo at elevated temperatures degradation by random scission of bonds with the lowest dissociation energy. This process could be accompanied by a non-chain-scission reaction leading to cross-linking.

If the degradation proceeds through a random chain-scission mechanism, chain fragments of lower molecular weight are formed which eventually will transform into volatile products. In the case of degradation connected with a cross-linking reaction, cyclization will take place leading to formation of nonvolatile carbonaceus structures (char).

Since thermogravimetry measures the formation of volatile products it is obvious that TGA does not provide means for selective monitoring of the various degradation steps. The apparent rate of degradation measured by the isothermal TGA is an average value of the overall process. Actually, if the degradation of a copolymer proceeds via the initial cleavage of more than one type of chemical bonds (groups) in the polymer chain, the monitoring and interpretation of the degradation process through TGA becomes even more difficult. In order to interpret the TGA data, it is helpful to compare the kinetic parameters obtained by the isothermal TGA of the model polymers with the kinetic data for the cleavage of urethane groups and oxazolidone and isocyanurate rings, determined on the model compounds using IR spectroscopy.

Urethane System. The Arrhenius plots of the rate constants for the degradation of PUR-I and UR-I are presented in Figure 14.

Table I

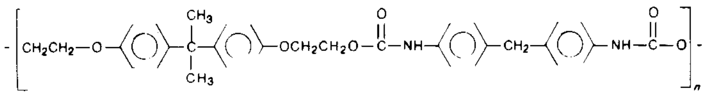
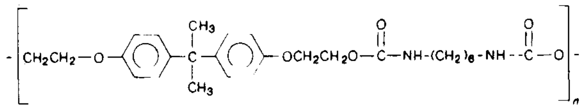
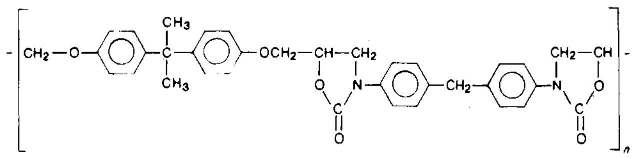
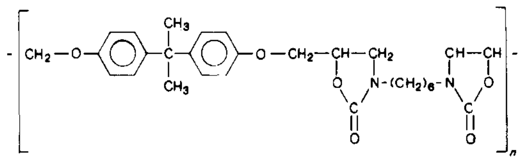
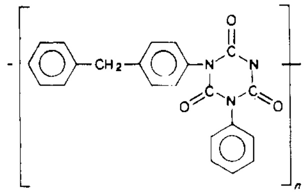
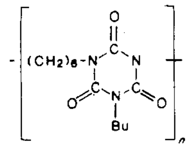
model polymer	structure
PUR-I	
PUR-II	
POX-I	
POX-II	
PTR-I	
PTR-II	

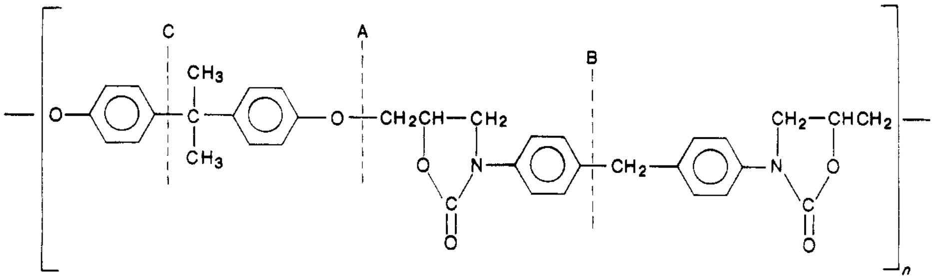
Table II
Kinetics of the Thermal Degradation of Model Polymers

model polym	viscosity, η_{inh}	T, °C	$k \times 10^3$, min^{-1}	E_a, kJ	A, min^{-1}	T_D[b]
PUR-I	0.436	260	0.775	184.1	9.00×10^{14}	284
		287	5.996			
		305	19.603			
PUR-II	0.517	276	4.732	167.6	3.01×10^{13}	282
		300	15.404			
		314	36.046			
		337	113.321			
POX-I	0.248	327	3.078	191.0	1.32×10^{14}	334
		355	17.843			
		378	61.488			
POX-II	0.314	327	1.978	212.2	6.40×10^{15}	339
		365	32.708			
		375	50.680			
		385	87.578			
PTR-I		405	0.991	184.1	1.41×10^{11}	441
		427	2.314[a]			
		447	6.726[a]			
PTR-II	0.31	410	4.078	246.7	3.54×10^{16}	410
		430	13.237			
		450	53.869			

[a] Initial rate. [b] T_D = temperature of decomposition at k = 0.005 min^{-1}.

This figure shows that the rates measured for the model polymer system were lower than the corresponding rates of the model compounds. From Table II we see that the activation energies for PUR-I (184.1 kJ) and UR-I (161.8 kJ)[13] were comparable, taking into account the different methods employed in each case. Consequently, a comparison of the data obtained by TGA and the IR technique shows that the degradation of the model polyurethane PUR-I proceeds through cleavage of the carbamate group as in the model compound, UR-I, and leads primarily to the formation of volatile products with no apparent cross-linking taking place (Figure 4).

Oxazolidone System. In the case of the oxazolidone, the Arrhenius rate constant plot for POX-I covers lower temperature regions than the Arrhenius plot of OX-I. This means that the model polymer decomposes faster than the model compound at the same temperature. This phenomenon can be explained if we assume that another scission in the polymer chain (besides the one of the oxazolidone ring) proceeds in the range of temperatures in



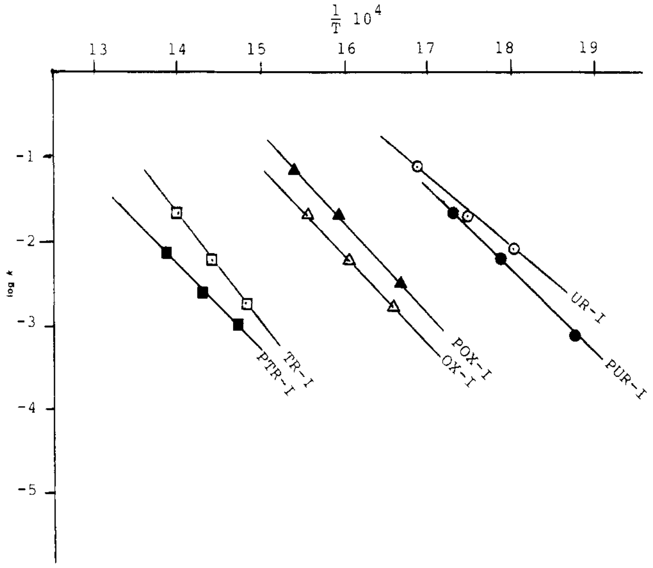
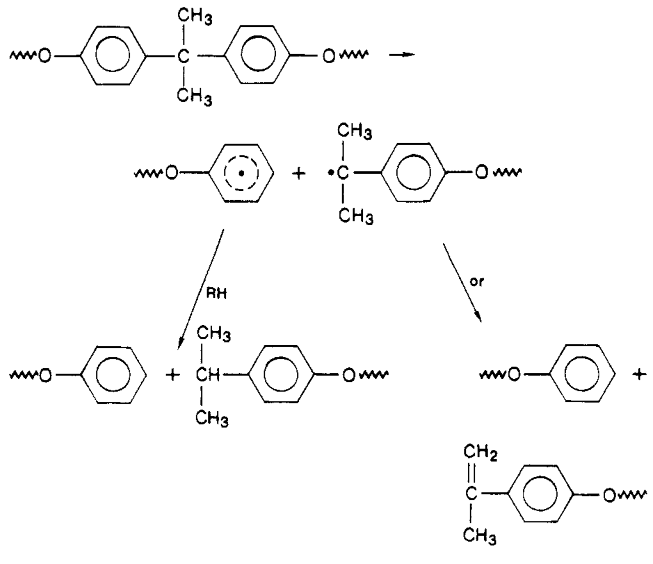


Figure 14. Arrhenius plots of model polymers and corresponding model compounds.

which the kinetic investigation was conducted.

A literature survey[21-26] showed that bond scission in the polymer chain of POX-I is confined almost exclusively to three sites, A, B, and C.

Bowen[22] and Paterson-Jones[21] determined that the scission of a bond in site A is taking place at temperatures higher than 360 °C. Similarly Freeman et al.[27] showed that aryl–methylene scission (site B) takes place at temperatures close to 450 °C. Leisegang[25] established that the scission of the aryl–isopropylidene bonds (site C) proceeds according to the following mechanism:



Bowen[22] and Danilina[28] showed also that this scission takes place quite rapidly at 350 °C; therefore the degradation of polyoxazolidones prepared from 2,2-bis[p-(2,3-epoxypropoxy)phenyl]propane is probably associated with aryl–isopropylidene scission as well as oxazolidone scission.

Isocyanurate System. In the case of PTR-I and TR-I, Figure 14 shows that the apparent rates of decomposition of PTR-I, measured by isothermal TGA, are lower than the corresponding rates of degradation of TR-I at the same temperatures. However, the activation energy of PTR-I (184.09 kJ) is much lower than the activation energy of TR-I (252.2 kJ).[13] This phenomenon can be explained if we assume that the degradation of PTR-I leads to a significant amount of cross-linking and formation of carbonaceous products (char). The results of the dynamic thermogravimetric analysis support this conclusion. Figure 6 shows that PTR-I lost only 60% of its weight in the dynamic TG analysis. Also on Figure 6, the deviation from first-order kinetics is associated with char formation. Further heating had very little effect on the weight loss.

This observation was in good agreement with the work of Winslow et al.[29] and Bruck[30,31] who showed that polymers with high concentrations of aromatic rings in their repeating unit degrade to form relatively small amounts of volatile products. The main degradation reaction led to fusion of the aromatic rings with formation of carbonaceous products (char). Korshak[19] also showed that the formation of nonvolatile carbonaceous products depends on the concentration of aromatic rings in the repeating unit of the polymer.

Conclusions

The thermostability of model block copolymers (urethanes, oxazolidones, and isocyanurates) was studied by dynamic and isothermal thermogravimetric analysis. The kinetic data obtained by isothermal TGA showed that the thermostability of the block copolymers (with similar block structure) increased in the following order: urethanes < oxazolidones < isocyanurates.

The comparison of the kinetic parameters (rate constants, activation energies) obtained by isothermal TGA with the kinetic data for the cleavage of the urethane groups and oxazolidone and isocyanurate rings determined by IR spectroscopy on the model compounds showed that in the case of urethane block copolymers the degradation proceeds through cleavage of the urethane groups. In the case of oxazolidone block copolymers it was established that the degradation probably proceeds by the parallel scission of the oxazolidone rings and aryl–isopropylidene bonds. The degradation of isocyanurates through cleavage of isocyanurate rings was complimented with a cross-linking, char-forming reaction.

The thermostability of urethane groups and oxazolidone and isocyanurate rings is affected by the neighboring substituent.

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Registry No. PUR-I (block copolymer), 109013-86-7; PUR-I (SRU), 52529-11-0; PUR-II (block copolymer), 109013-87-8;

PUR-II (SRU), 76709-95-0; POX-I (block copolymer), 109013-89-0; POX-II (block copolymer), 109013-88-9; PTR-I (block copolymer), 109013-91-4; PTR-II (block copolymer), 109013-90-3; $OCNC_6H_5$, 103-71-9; 4,4′-$OCNC_6H_4CH_2C_6H_4NCO$, 101-68-8; $OCN(CH_2)_6NCO$, 822-06-0; BuNCO, 111-36-4; $OCNC_6H_{10}CH_2C_6H_{10}NCO$, 5124-30-1; $C_6H_{11}NCO$, 3173-53-3.

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Dipole Orientation in a Liquid-Crystal Polymer: A Study by Electric Field FTIR

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ABSTRACT: A dynamic study of dipole alignment in a main-chain liquid-crystal polymer exposed to an electric field revealed some fundamental properties of these macromolecules. The polymer studied was the polycondensate of 40 mol % poly(ethylene terephthalate) and 60 mol % *p*-acetoxybenzoic acid. Spectroscopic analysis of attenuated infrared reflections during application of an electric field allowed us to measure the spatial alignment of ester dipole moments. When poling occurs before or during the solid to liquid-crystal transformation, one observes a relatively fast dielectric alignment which remains stable in the liquid-crystal phase. When the liquid crystal is solidified under the field the extent of polar alignment for moments nearly orthogonal to the backbone could lie in the range of 4–10%. This range suggests that interchain dipolar coupling is an important phenomenon in these polymers. On this basis one may also expect that localized ferroelectric ordering enhances cooperative behavior during the transition from "poled" solid to liquid crystal. The observed phenomena could be useful in the formation of polymeric solids with electrical or nonlinear optical properties.

Introduction

Weak external fields can induce long-range molecular reorientation in liquid crystals.[1,2] The field-induced molecular alignment disappears for the most part after crystallization occurs at lower temperatures. However, when the molecules of the liquid crystal have polymeric dimensions it might be possible in some cases to freeze the alignment in the solid state. Long relaxation times and the absence or slow rate of three-dimensional crystallization are among the factors that may allow vitrification of the aligned state. The frozen orientational order could be significant since polymeric mesophases have high order parameters and are suspected to have lower symmetries than their small molecule analogues. Thus it might be possible to form microstructures with anisotropic properties after the vitrification or crystallization of polymer liquid crystal fluids aligned by electric, magnetic, flow, or surface fields. Our group reported previously on studies of backbone orientation by magnetic,[3] electric,[4] and surface fields[5] in main-chain liquid-crystal polymers. The present work focuses on field orientation on a finer scale, namely, the electric orientation of dipoles contained within the self-ordering rigid chains. The problem is of interest in the area of advanced polymers, given the special properties exhibited by poled solid phases. These include, among others, nonlinear optical properties and piezo- and pyroelectricity.

As predicted by the Langevin equation, low molecular weight polar fluids will experience only weak alignment even in strong electric fields. Field orientation of dipoles in a condensed phase which is both "polymeric" and "liquid crystalline" is a more complex and poorly understood phenomenon. In the high order parameter mesophases formed by polymers, it is not known if self-ordering characteristics would extend to a finer structural scale such as that of dipoles that are orthogonal or parallel to the backbone. It is this particular question that we have addressed in this paper. The measurements carried out

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