the shape of the transition curve and the effect of N are all preserved as they have been discussed in Figure 3. A close inspection may reveal that the transition curves are asymmetric, especially at low N's, around the center of the RH $\alpha \rightarrow$ LH α transition. For example, the curve at $N = 100$ changes almost linearly with T on the coil side while remaining nearly flat on the helix side. This observation may allow a crude conjecture of the direction of the helix–coil transition.

IV. Concluding Remarks

In this study we have expanded the Zimm–Bragg–Nagai model[1,4,5] for the helix–coil transition to develop a theory applicable to the helix-sense inversion observed for poly(L-aspartate esters).[11] We have allowed each peptide residue to adopt three conformational states, i.e., RH α, LH α, and coil states, and have derived formal expressions for average fractions of helical conformers in terms of S, σ, and N. The key assumption in the present theory is that the conformational state of a given residue is influenced by those of neighboring residues. The hydrogen-bond formation and the side-chain nonbonded interaction are discussed as the factors responsible for this interaction, and it is shown that they exclude the occurrence of certain unfavorable sequences. Among excluded sequences those involving consecutive rl units are especially important, since their absences mean that the sense inversion proceeds accompanied by at least one coil residue between RH and LH α-helical sequences. In other words, the inversion is driven by a competition between tendencies to form RH and LH α-helices from coil residues. An ill-defined, molecular-order RH $\alpha \rightleftharpoons$ LH α equilibrium is thus reinterpreted in our model by the coexistence of two equilibria, RH $\alpha \rightleftharpoons$ coil and coil $\rightleftharpoons$ LH α, in the residual order.

In this paper we have restricted ourselves to establishing a model relevant to the sense inversion. Formulas are derived only for the conformer's fractions, although the theory can further be expanded to obtain other averages such as the length and the number of helical sequences. These quantities should be of importance in penetrating into the detailed mechanism of the sense inversion. An experimental determination of the $f_r - f_l$ vs. N relationship is also needed for a critical test of the theory. Nevertheless, even in the absence of these informations, fundamental aspects of the sense inversion can well be elucidated by the present model on the basis of calculated transition curves and their comparison with the previous observations for PPELA.[11]

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Mechanism of Thermal Degradation of Polyurethanes. Effect of Ammonium Polyphosphate

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ABSTRACT: The thermal decomposition of some structurally related N–H and N-substituted polyurethanes and their mixtures with ammonium polyphosphate (APP) was investigated by thermogravimetry (TG) and direct pyrolysis in a mass spectrometer (MS). The N–H polyurethanes (I–III) undergo a quantitative depolymerization process with formation of compounds with amine and isocyanate end groups. On the other hand, the thermal degradation of the N-substituted polyurethanes (IV–IX) proceeds by a different mechanism as a function of their chemical structure. Three thermal degradation pathways have been ascertained: N–H hydrogen transfer (I–III), β-CH hydrogen transfer (IV–VII), and α-CH hydrogen transfer (V, VI, VIII, and IX). The addition of APP lowers the thermal stability of N-substituted polyurethanes V, VI, VIII, and IX, whereas that of the other polymers remains unaltered. Our data show that APP often changes the nature of the pyrolytic products, sometimes inducing a hydrolytic cleavage of the polymer chain and sometimes causing the formation of tertiary amines.

Introduction

Direct pyrolysis of polymers in the mass spectrometer (DP–MS) is an excellent method for monitoring the initial thermal fragmentation processes occurring when polymers are heated to decomposition.[1] We have investigated several classes of polymers by the DP–MS method[2–4,9] as a part of our longer term investigation of the primary thermal fragmentation processes of polycondensates.

Previous MS studies have shown that N–H substitution

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affects drastically the primary thermal fragmentation processes in polyurethanes.[3] N-Substituted polyurethanes containing an aliphatic chain adjacent to the oxygen atom (i.e., made from an aliphatic dialcohol) were found to decompose thermally through an intramolecular hydrogen-transfer reaction producing olefin, secondary amine, and carbon dioxide. In totally aromatic N-substituted polyurethanes the formation of cyclic oligomers in the primary thermal fragmentation has been ascertained.[3] Therefore the thermal degradation pathways of these polymers appear to be strongly influenced by structural factors.

In the present work we report a study of the effect of ammonium polyphosphate (APP) on the thermal stability of some N–H and N-substituted polyurethanes (Table I).

There are accounts in the literature dealing with the mechanism of action of APP on the thermal decomposition of some polymeric substrates,[4–9] and it is generally agreed that APP, a precursor of poly(phosphoric acid), is capable of lowering the thermal stability of these polymers, presumably because it promotes acid-hydrolytic reactions of the substrates.[9]

Our results show that the mechanism of thermal decomposition of polyurethanes depends on the structure of each polymer (Table I), and therefore the presence of APP affects them in different ways.

Experimental Section

Materials. The bis(chloroformates) of neopentyl glycol and 4,4′-isopropylidenediphenol were prepared in toluene from the appropriate dihydroxy compound and phosgene, with triethylamine as an acceptor of HCl; the first had bp 75 °C (0.5 torr) and the second had mp 97–98 °C. 4,4′-Methylenebis(*N*-methylaniline) was prepared by the method of Fedotova et al.[10] Other materials were commercial products appropriately purified before use.

Polymerization was carried out by dispersion polycondensation. In a typical procedure, 1 g (0.0116 mol) of piperazine and 2.46 g (0.0232 mol) of Na_2CO_3 in 25 mL of water were placed in a Waring blender, precooled in a freezer. To the rapidly stirred system was added 2.663 g (0.0116 mol) of neopentyl glycol bis(chloroformate) in 20 mL of tetrahydrofuran, in one application. The mixture was stirred for 5 min and poured into about 300 mL of cold water. After some hours, the polymer was filtered, washed with water, and dried in vacuo at 70 °C.

Ammonium polyphosphate (APP) was obtained from Hoechst (Exolit 263). Mixtures were prepared by combining polyurethane mechanically with 10% APP in a porcelain mortar.

Viscometry. Inherent viscosities of polymers ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) were measured in a Desreux–Bishoff suspended-level viscometer that contained a coarse sintered-glass filter attached just below the reservoir through which the solutions passed as they rose into the capillary. The temperature was maintained at 30 ± 0.01 °C. Pertinent values are reported in Table I.

Thermogravimetry. A Perkin-Elmer thermal analyzer TGS-2 was used to determine the thermal behavior of the samples. Experiments were carried out on about 2 mg of sample under nitrogen (flow rate 60 mL/min) and a furnace heating rate of 10 °C/min up to 750 °C.

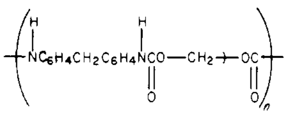
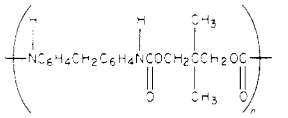
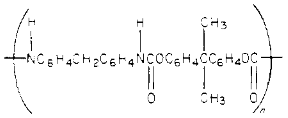
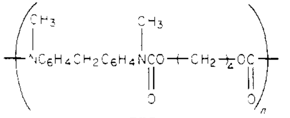
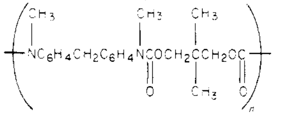
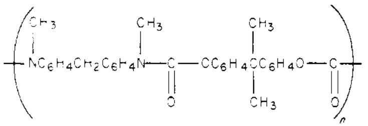
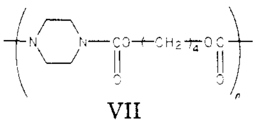
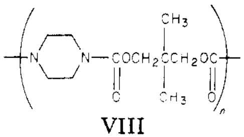
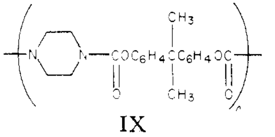
Mass Spectrometry. Pyrolyses were carried out in quartz probes with the direct insertion inlet of an electron impact mass spectrometer LKB 9000 S according to a technique described elsewhere;[1] the heating rate was about 10 °C/min. Mass spectra were obtained at 18 eV.

Results and Discussion

Thermogravimetry. To characterize the thermal stability of the polyurethanes I–IX and relative mixtures with APP, TG experiments under N_2 flow and a heating rate of 10 °C/min were performed.

Temperatures of maximum rate of polymer degradation (PDT) of polyurethanes are reported in Table I. The thermal stability of N-substituted polyurethanes IV–IX appears to be higher than that of the N–H polymers I–III.

Table I
Structure, Maximum of Polymer Degradation Temperature (PDT), and Inherent Viscosity of the Polyurethanes Investigated

		PDT values[d]	
polymer structure	η_{inh},[a] dL/g	pure	with 10% APP
 I	0.29[b]	325	305
 II	0.28[b]	330	310
 III	0.33[b]	285	285
 IV	0.16[b]	395	380
 V	0.14[b]	480	380
 VI	0.27[b]	490	435
 VII	0.94[c]	370	370
 VIII	0.93[c]	460	400
 IX	1.10[c]	480	420

[a] $\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL. [b] In dimethylformamide. [c] In 3:2 (v/v) phenol–tetrachloroethane. [d] TG experiments under N_2, flow rate 60 mL/min, heating rate 10 °C/min.

Comparing the PDT values of the pure and APP-doped polyurethanes, one can note that the thermal decomposition temperature of N-substituted polyurethanes having a PDT higher that 370 °C is lowered by the presence of APP.

Mass Spectrometry. To investigate at the molecular level the mechanism of action of APP on the thermal degradation of polyurethanes I–IX, direct pyrolysis in the mass spectrometer was carried out. In this technique,[1] polymers are introduced via the direct insertion probe and the temperature is increased gradually to a point at which thermal degradation reactions occur; the volatile compounds formed are then ionized and detected. The mass

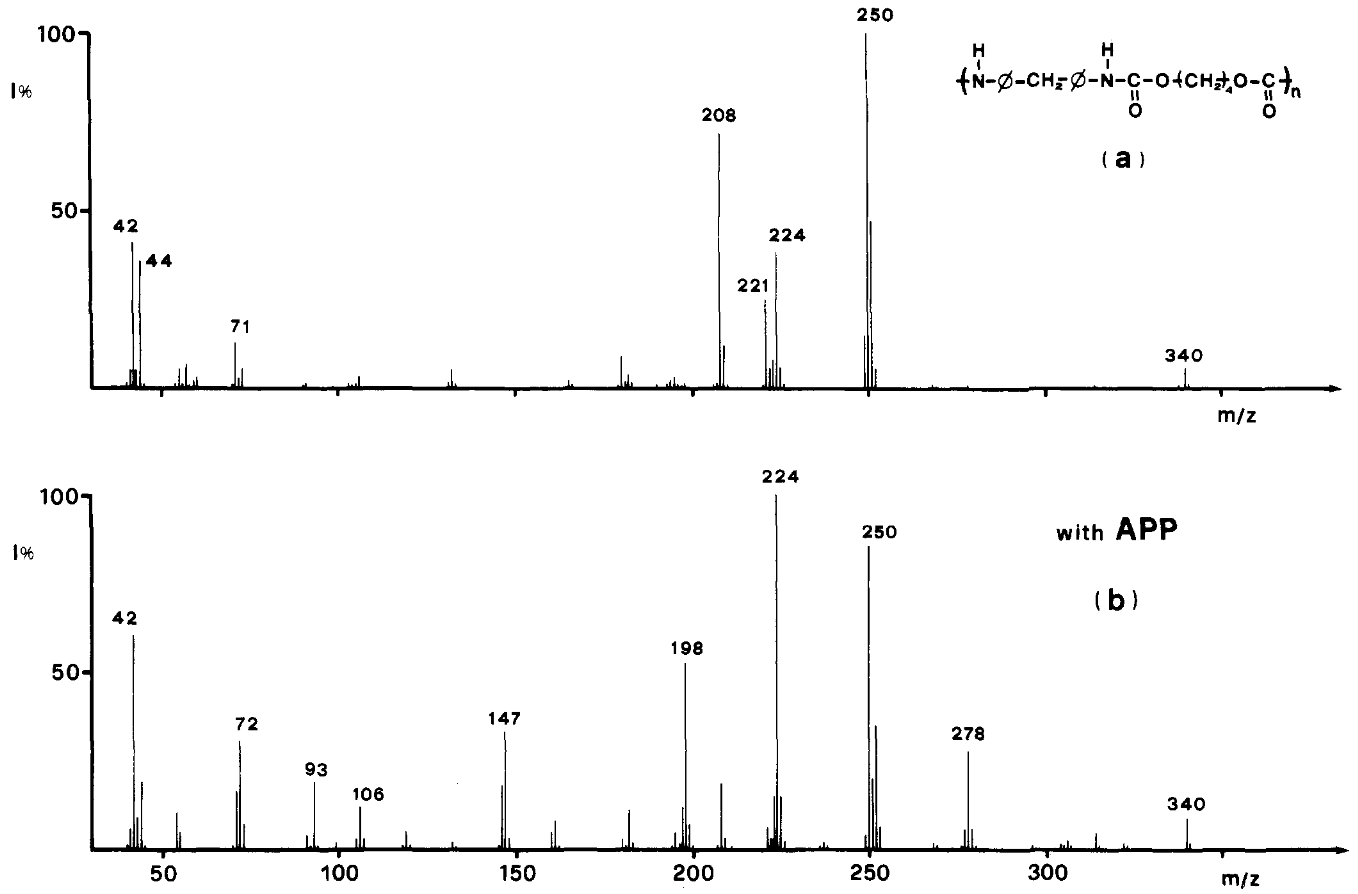


Figure 1. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane I at a probe temperature of 330 °C and (b) polyurethane I–APP (10%) mixture at 310 °C.

spectrum of the polymer obtained under these conditions is therefore that of the mixture of compounds formed by pyrolysis.

A general advantage of this technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal fragments formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collisions and fast detection, reduces to a great extent the occurrence of secondary reactions, so that almost exclusively primary fragments are detected. Furthermore, fragments of high mass, by which the degradation processes are often diagnosed, can be detected, whereas they are lost in other techniques.

Polymer I. Figure 1a shows the mass spectrum of polyurethane I recorded at a probe temperature of 330 °C. The spectrum appears to be essentially that of a mixture of 4,4′-methylenebis(phenyl isocyanate) (MDI) and 1,4-butanediol. In fact, the base peak at *m/z* 250 corresponds to the molecular ion of MDI, and peaks at *m/z* 221, 208, and 106 are EI fragments originating from it. The molecular ion of the butanediol is absent, but typical EI fragments appear at *m/z* 71, 44, and 42.

Figure 1b shows the mass spectrum of the polyurethane I–APP mixture at 310 °C. When this spectrum is compared with that in Figure 1a, a strong difference in the relative abundance of several peaks and also the appearance of some new peaks can be noted.

The base peak (*m/z* 224) corresponds to (4-aminophenyl)(4-isocyanophenyl)methane, the partial hydrolysis product of MDI. The intense peak at *m/z* 198 corresponds to bis(4-aminophenyl)methane (4,4′-diaminodiphenylmethane, DADPM), and the peak at *m/z* 93 corresponds to aniline, originating from the hydrolytic cleavage of DADPM.

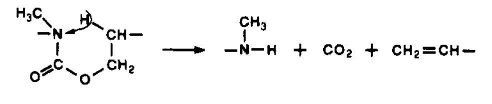
The overall evidence indicates that APP is inducing a hydrolytic cleavage of the polymer chains. However, MDI (*m/z* 250) still appears as an intense peak in the spectrum. Considering the moderate reduction of thermal stability induced by APP (Table I), one can infer that the hydrolytic process promoted by APP and the N–H hydrogen-transfer process occur competitively to the same extent.

Polymers II and III. The mass spectral data obtained for polymes II and III (Table I) are in agreement with those reported in the literature. As with polyurethane I, the thermal degradation process of these polymers involves an N–H hydrogen transfer to the oxygen atom with breakdown of the polymer chain and formation of compounds with isocyanate and hydroxyl end groups.

Comparison of the mass spectra with those of mixtures of both polymers with APP does not reveal changes in the pyrolytic products. Data in Table I show also that the thermal stability of these polyurethanes is little affected by the presence of APP.

Polymer IV. Figure 2a shows the mass spectrum of polyurethane IV recorded at a probe temperature of 395 °C. The structures of the intense ions at *m/z* 226, 324, 422, 594, and 692 are given in Table II.

All these fragments are molecular ions of compounds characterized by secondary amine and/or olefinic end groups originating through a β-CH hydrogen-transfer process, according to eq 1:



(1)

Figure 2b shows the mass spectrum of the polyurethane IV–APP mixture at 380 °C. Comparing this spectrum with that in Figure 2a, a strong difference in the relative

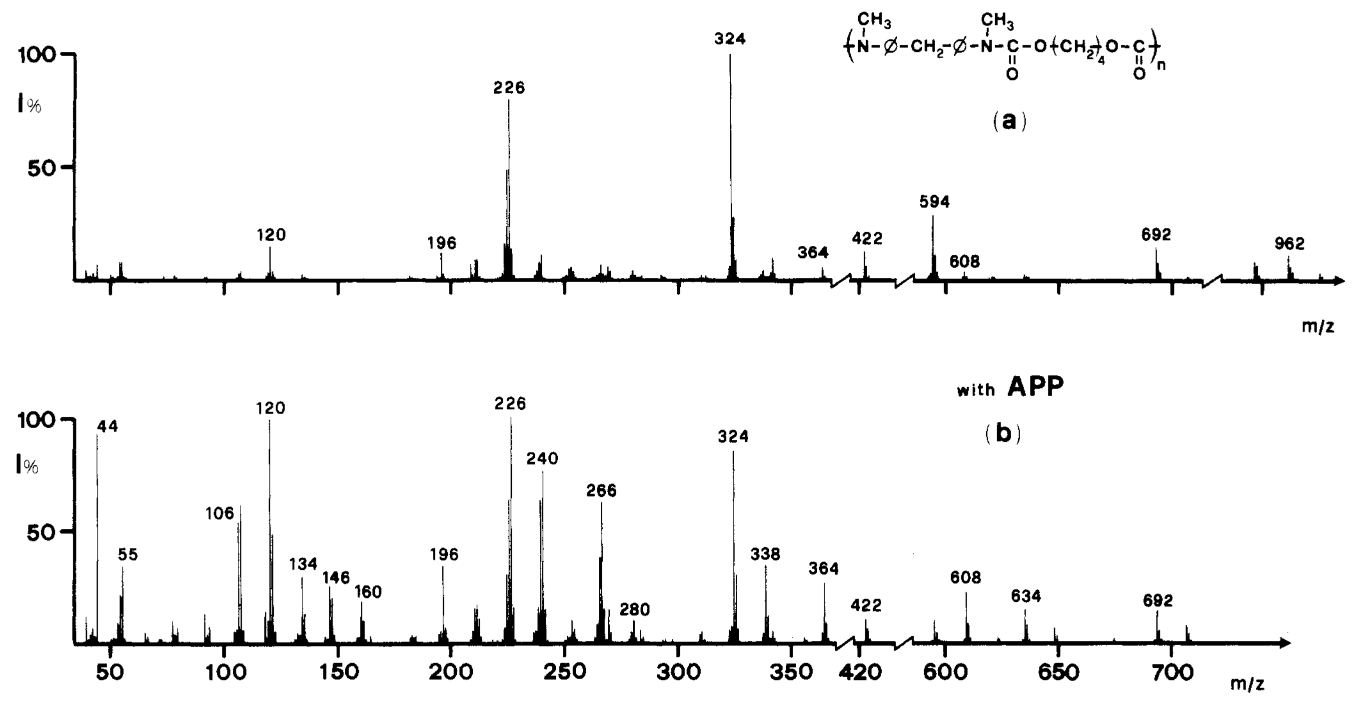


Figure 2. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane IV at a probe temperature of 395 °C and (b) polyurethane IV–APP (10%) mixture at 380 °C.

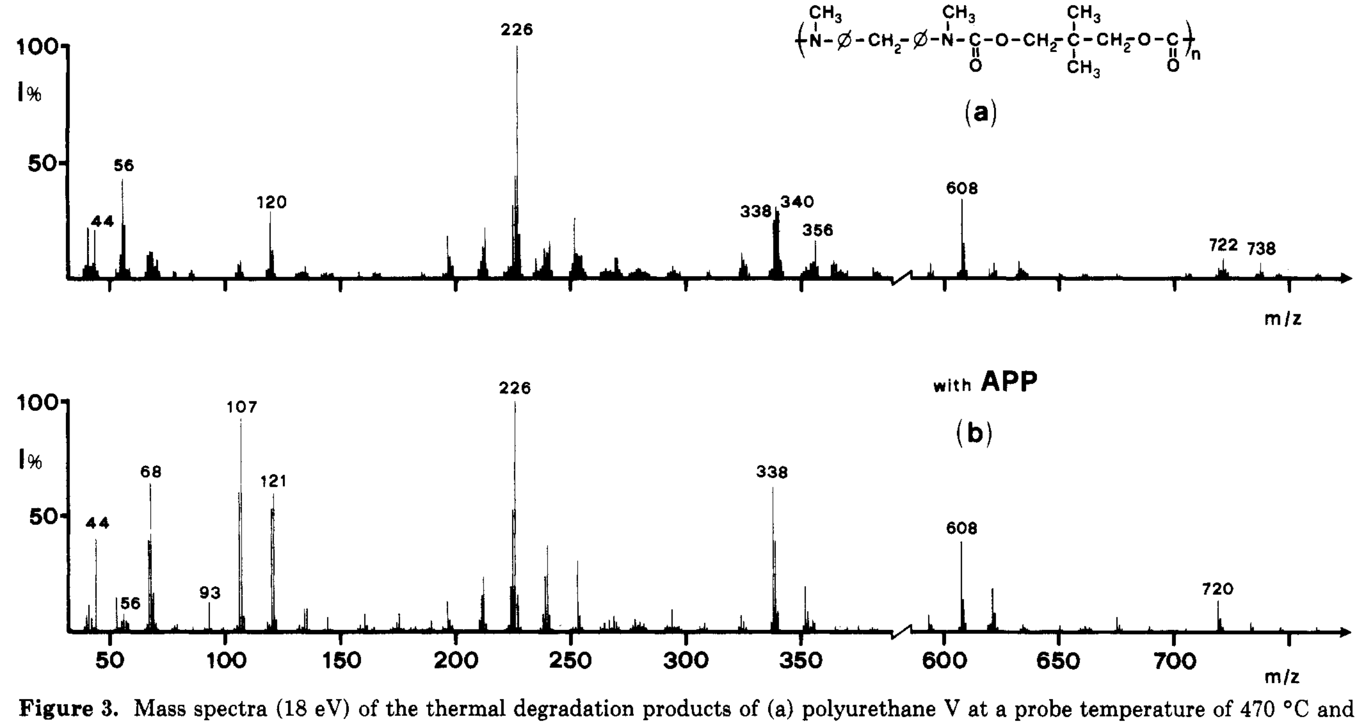
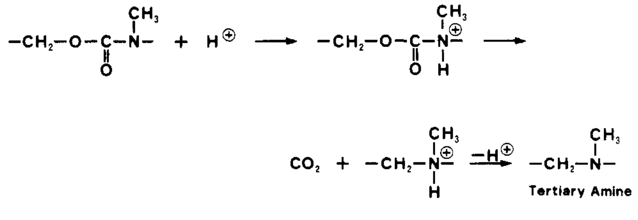


Figure 3. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane V at a probe temperature of 470 °C and (b) polyurethane V–APP (10%) mixture at 380 °C.

abundance of several peaks can be noted and also the appearance of some intense peaks corresponding to tertiary amines (Table II) and carbon dioxide, according to Scheme I. It has been suggested[11] that a recombination reaction leading to tertiary amines might be operative in the thermal degradation of pure N-substituted polyurethanes. Some evidence for the formation of tertiary amines in the pyrolysis of pure polyurethane IV might be found in the mass spectrum in Figure 2a but, without the comparison with the spectrum obtained in the pyrolysis catalyzed by APP (Figure 2b), it would have remained ambiguous. Typical tertiary amine EI fragments are present in the spectrum at *m/z* 106, 120, 146, and 160.

Scheme I



The formation of tertiary amines promoted by APP becomes competitive with the β-hydrogen-transfer process, but it does not become preponderant. This fact is reflected

Table II
Molecular Ions and EI Fragments of Compounds Formed in the Pyrolysis of Polyurethane IV

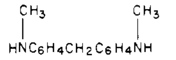
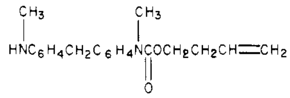
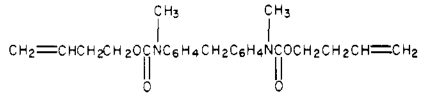
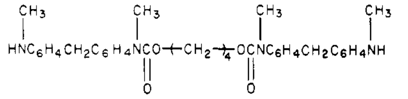
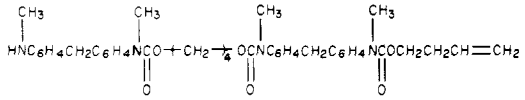
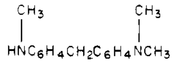
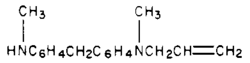
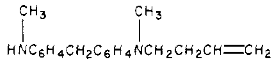
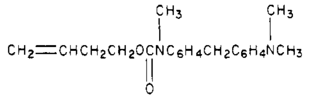
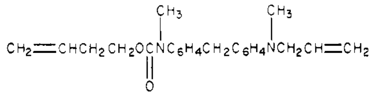
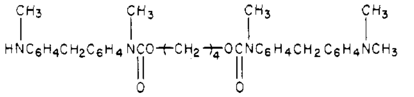
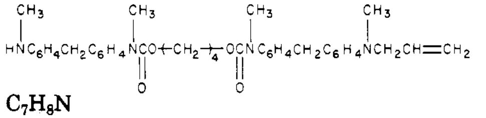
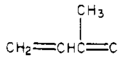
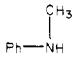
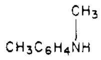
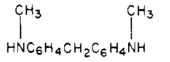
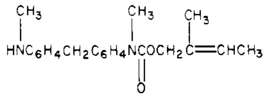
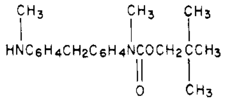
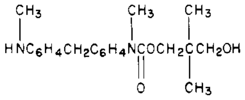
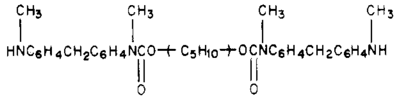
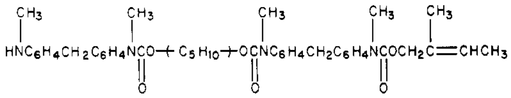
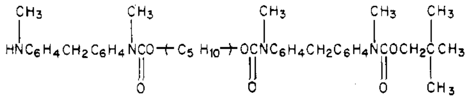
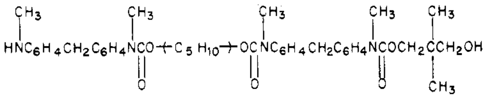
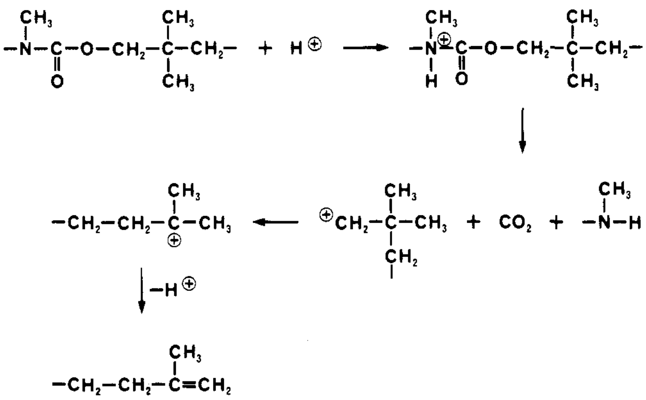
fragment$^+$	m/z
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}H$	226
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2CH_2CH{=}CH_2$	324
 $CH_2{=}CHCH_2CH_2O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2CH_2CH{=}CH_2$	422
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(CH_2)_4O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}H$	594
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(CH_2)_4O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2CH_2CH{=}CH_2$	692
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_3$	240
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_2CH{=}CH_2$	266
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_2CH_2CH{=}CH_2$	280
 $CH_2{=}CHCH_2CH_2O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_3$	338
 $CH_2{=}CHCH_2CH_2O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_2CH{=}CH_2$	364
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(CH_2)_4O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_3$	608
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(CH_2)_4O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}CH_2CH{=}CH_2$	634
C_7H_8N	106
$C_8H_{10}N$	120
$C_{10}H_{12}N$	146
$C_{11}H_{14}N$	160

Table III
Molecular Ions and EI Fragments of Compounds Formed in the Pyrolysis of Polyurethane V

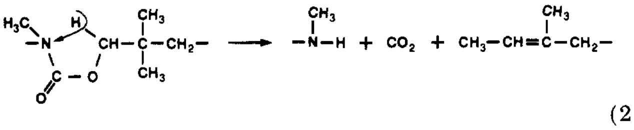
fragment$^+$	m/z
 $CH_2{=}CH\overset{CH_3}{C}{=}CH_2$	68
Ph-NH$_2$	93
 $Ph{-}\overset{CH_3}{N}H$	107
 $CH_3C_6H_4\overset{CH_3}{N}H$	121
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}H$	226
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2\overset{CH_3}{C}{=}CHCH_3$	338
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_3$	340
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2OH$	356
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(C_5H_{10})O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}H$	608
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(C_5H_{10})O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2\overset{CH_3}{C}{=}CHCH_3$	720
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(C_5H_{10})O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_3$	722
 $H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}O(C_5H_{10})O\underset{O}{C}\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{C}OCH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2OH$	738

Scheme II



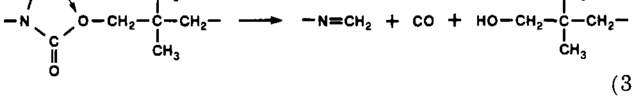
by the little effect that the presence of APP has on the thermal stability of polyurethane IV (Table I).

Polymer V. Figure 3a shows the mass spectrum of polyurethane V recorded at a probe temperature of 470 °C. The structural assignments of the most intense ions observed in the spectrum are given in Table III. The presence of fragments characterized by secondary amine and/or C_5H_9 end groups (m/z 720, 608, 338, and 226) indicates that the thermal degradation of polymer V occurs via a mechanism that involves an α-CH hydrogen transfer and an intramolecular methyl shift, as illustrated in eq 2:

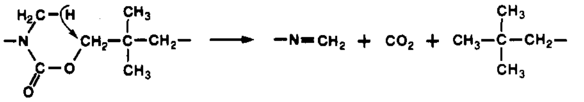


(2)

In addition to the process discussed above, the occurrence of some other thermal decomposition processes is suggested by the presence in the spectrum of peaks (m/z 738, 722, 356, and 340) that contain alcoholic or aliphatic end groups (see Table III), according to eq 3 and 4:



(3)



(4)

The molecular ion of the neopentyl glycol that should be formed according to eq 3 is absent in the spectrum, but a typical EI fragment appears at m/z 56.

Figure 3b shows the mass spectrum of the polymer V–APP mixture at 380 °C. Comparing this spectrum with that in Figure 3a, the increment of peaks at m/z 720, 608, 338, and 226 and the appearance of a series of intense peaks at low masses (m/z 121, 107, 93, and 68) can be noted.

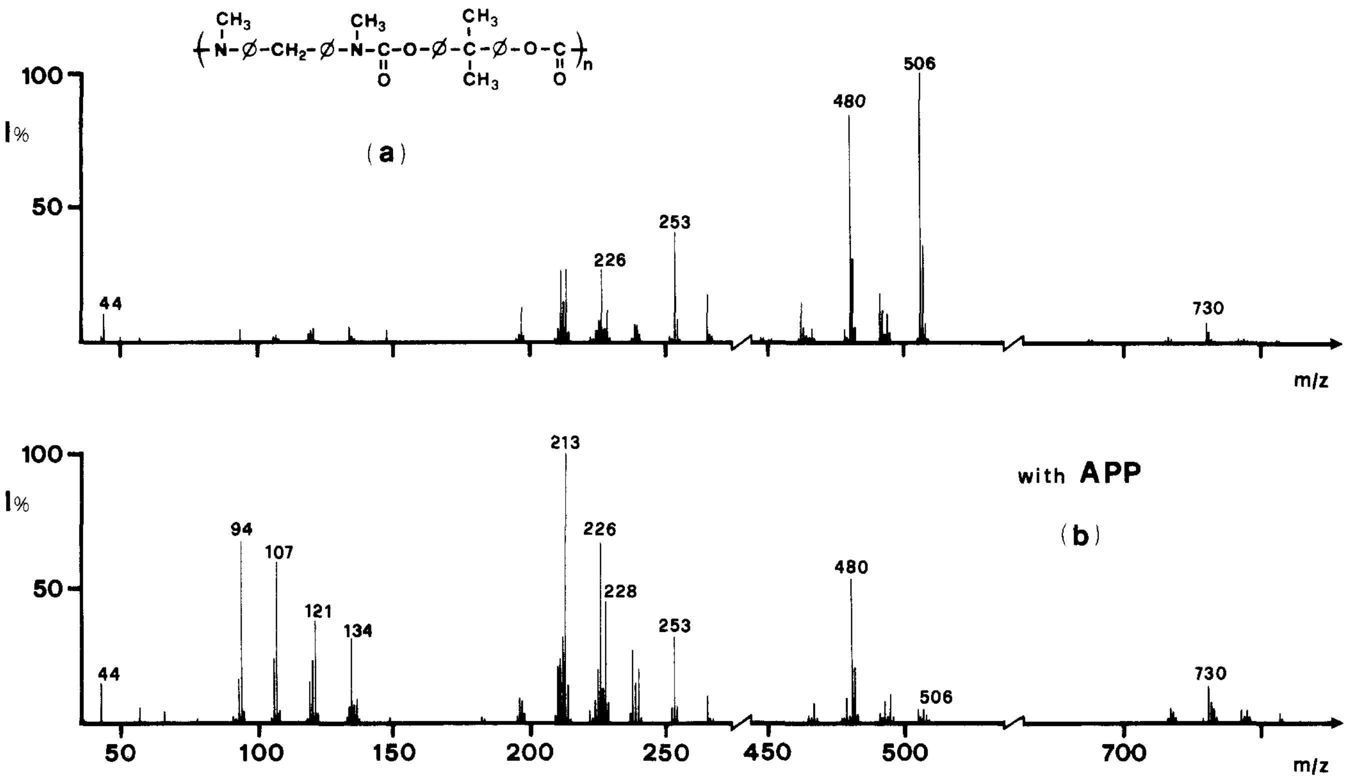


Figure 4. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane VI at a probe temperature of 490 °C and (b) polyurethane VI–APP (10%) mixture at 450 °C.

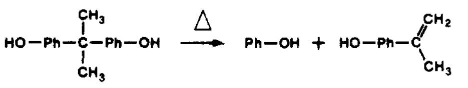
All these fragments, identified in Table III, possess amino and/or olefin end groups, suggesting that APP, inducing the protonation of the nitrogen atom (Scheme II), catalyzes selectively the process illustrated in eq 2. This determines the breakdown of the polymer chain at an enhanced rate, as confirmed by the strong reduction of the thermal stability induced by APP on this polymer (Table I).

Polymer VI. Figure 4a shows the mass spectrum of polyurethane VI recorded at a probe temperature of 490 °C.

The structural assignments of the two more intense ions, at *m/z* 506 and 480, are given in Table IV. The peak at *m/z* 506 has been identified as a cyclic oligomer, indicating that the thermal degradation of polymer VI occurs by an ester exchange process.[3] The peak at *m/z* 480 corresponds to open-chain oligomer formed by hydrolytic cleavage of the polymer chain.

Figure 4b shows the mass spectrum of the polyurethane VI–APP mixture at 450 °C. Comparing this spectrum with that in Figure 4a, the remarkably low intensity of the cyclic oligomer at *m/z* 506 and the increased intensity of fragments with phenolic (*m/z* 480, 228, and 94) and amino (*m/z* 226, 121, and 107) end groups (Table IV) can be noted. This indicates that APP catalyzes the hydrolytic cleavage of the polyurethane chain, and, consequently, the breakdown of the polymer chain occurs at lower temperatures (see Table I).

In Figure 4b peaks at *m/z* 94 and 134, respectively, appear strongly enhanced, implying that another thermocleavage process, catalyzed by APP, occurs in this polymer (eq 5):

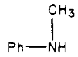
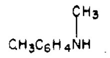
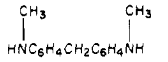
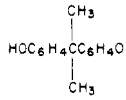
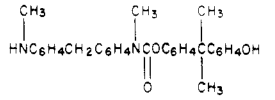
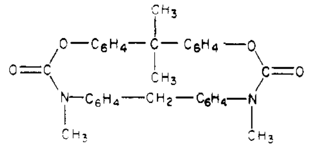


$$\mathrm{HO{-}Ph{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Ph{-}OH} \xrightarrow{\Delta} \mathrm{Ph{-}OH} + \mathrm{HO{-}Ph{-}C}\begin{matrix}\mathrm{{\diagup}CH_2}\\ \mathrm{{\diagdown}CH_3}\end{matrix} \qquad (5)$$

In fact, it is known[12] that the pyrolysis of 4,4′-isopropylidenediphenol produces almost equimolecular amounts of phenol and isopropenylphenol essentially through an acid-catalyzed disproportionation reaction.

Table IV

Molecular Ions and EI Fragments of Compounds Formed in the Pyrolysis of Polyurethane VI

fragment⁺	m/z
Ph-OH	94
 $\mathrm{Ph{-}\overset{CH_3}{N}H}$	107
 $\mathrm{CH_3C_6H_4\overset{CH_3}{N}H}$	121
 $\mathrm{H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}H}$	226
 $\mathrm{HOC_6H_4\underset{CH_3}{\overset{CH_3}{C}}C_6H_4OH}$	228
 $\mathrm{H\overset{CH_3}{N}C_6H_4CH_2C_6H_4\overset{CH_3}{N}\underset{O}{\overset{\Vert}{C}}OC_6H_4\underset{CH_3}{\overset{CH_3}{C}}C_6H_4OH}$	480
	506

Polymer VII. Figure 5a shows the mass spectrum of polyurethane VII recorded at a probe temperature of 370 °C. The inspection of the spectrum reveals the presence of two series of peaks respectively at *m/z* 314, 412, 542, 640, and 770 and at *m/z* 58, 84 (base peak), 284, 286, 512, and 514 corresponding to molecular ions of compounds formed by the pyrolysis of polymer chain. The structural assignments of these two series of ions are given in Table V.

The nature of these fragments implies that the thermal degradation of polyurethane VII occurs by two competitive reactions: the first is a β-hydrogen-transfer process with formation of compounds having piperazine and/or olefinic

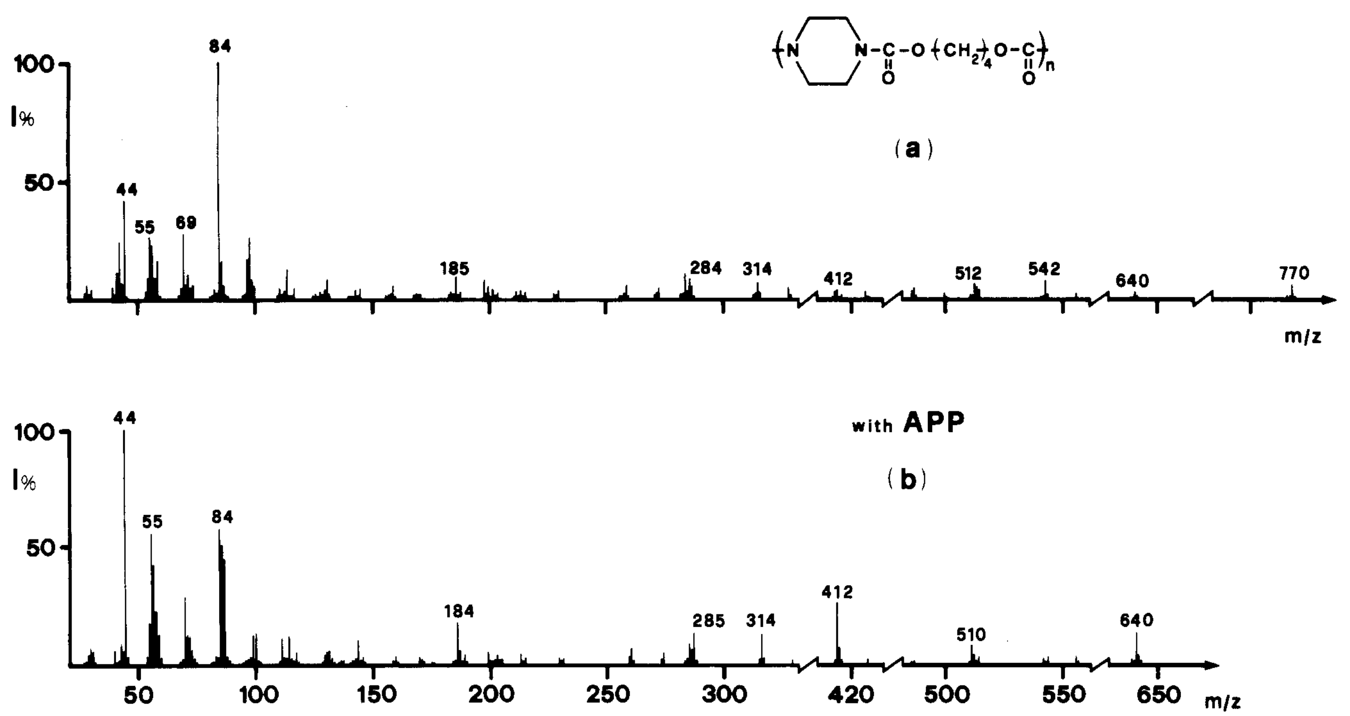
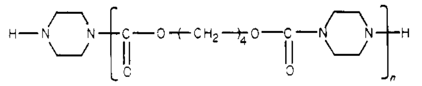
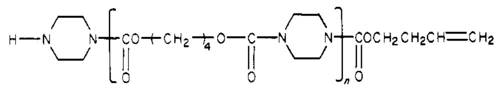
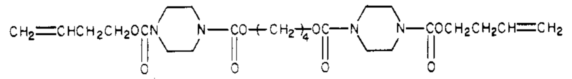
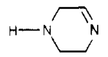
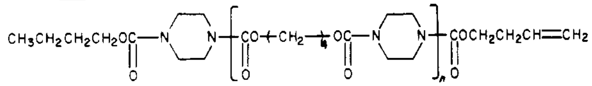
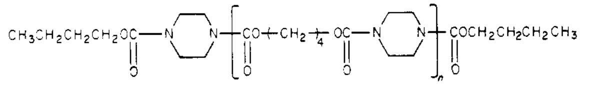
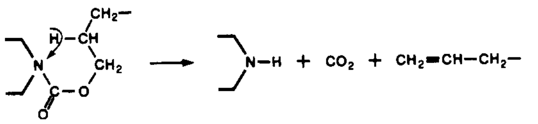


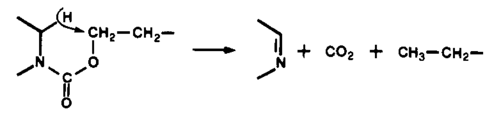
Figure 5. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane VII at a probe temperature of 370 °C and (b) polyurethane VII-APP (10%) mixture at 370 °C.

Table V
Molecular Ions and EI Fragments of Compounds Formed in the Pyrolysis of Polyurethane VII

fragment$^+$	m/z (n)
	86 (0), 314 (1), 542 (2), 770 (3)
	184 (0), 412 (1), 640 (2)
	510
$CH_3CH_2CH{=}CH_2$	56
$CH_3CH_2CH_2CH_3$	58
	84
	284 (0), 512 (1)
	286 (0), 514 (1)

end groups (eq 6); the second consists of the transfer of the hydrogen atom of the α-methylene group attached to nitrogen atom, according to eq 7:

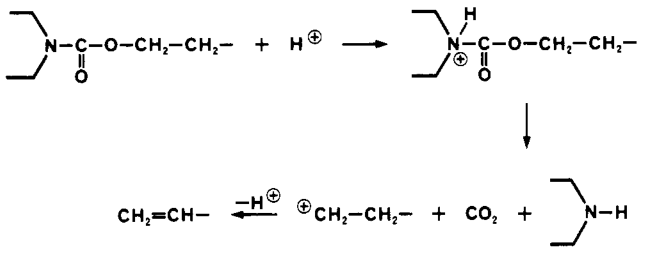

(6)


(7)

The latter process is strongly supported by the presence of the peak at m/z 84 (base peak) spectrum in Figure 5a.

Figure 6b shows the mass spectrum at 370 °C of the polymer VII–APP mixture. A reduction of the abundance of the peaks at m/z 84, 286, 512, and 514 and an increment of the peaks at m/z 44, 86, 184, 314, 412, 510, and 640 with respect to pure polyurethane VII are observed. This indicates that APP, by protonation of the urethane linkage, catalyzes selectively the β-CH hydrogen transfer as illustrated in Scheme III.

Scheme III



Polymer VIII. Figure 6a shows the mass spectrum of polyurethane VIII recorded at a probe temperature of 460 °C. Among the peaks observed in the spectrum, the presence of fragments at m/z 86, 198, 328, 440, 570, and 682, corresponding to molecular ions of compounds formed

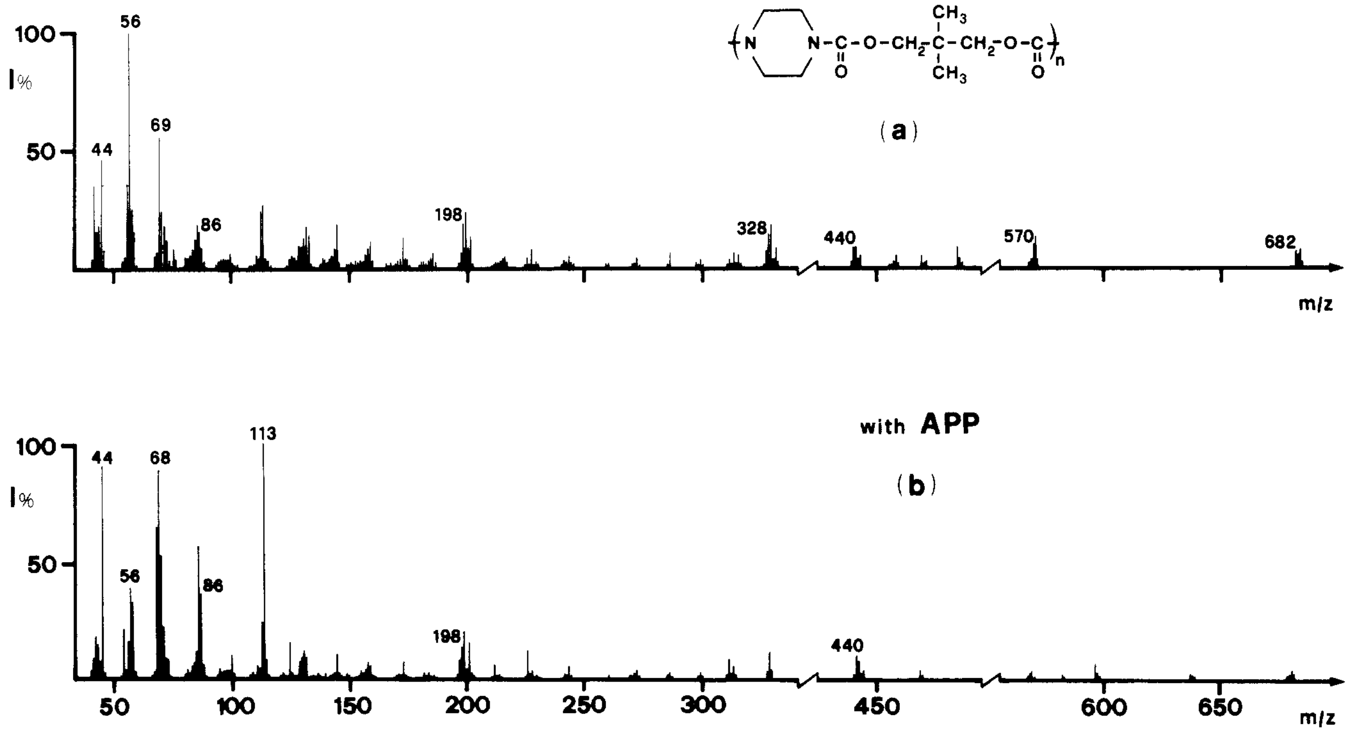
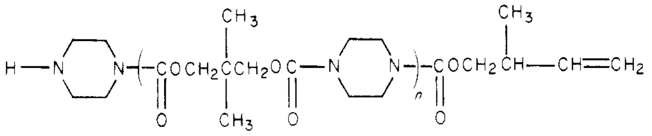
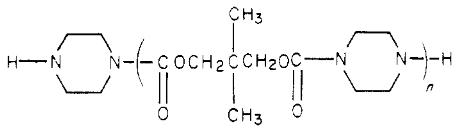


Figure 6. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane VIII at a probe temperature of 460 °C and (b) polyurethane VIII–APP (10%) mixture at 400 °C.

by the pyrolysis of the polymer can be noted. The structures that can be assigned to these compounds are as follows:



m/z (*n*): 198 (0), 440 (1), 682 (2)



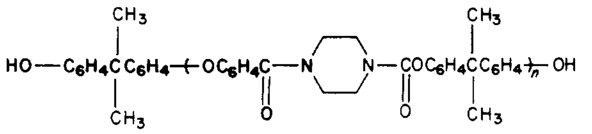
m/z (*n*): 86 (0), 328 (1), 570 (2)

The formation of these compounds implies that the pyrolysis occurs via an α-CH hydrogen transfer and an intramolecular methyl shift as in the polyurethane V (eq 2).

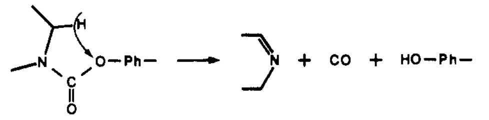
Figure 6b shows the mass spectrum of the polyurethane VIII–APP mixture at a probe temperature of 400 °C. Comparing this spectrum with that of the pure polyurethane (Figure 6a), an increment of the abundance of peaks at lower mass values can be noted.

Considering the reduction of thermal stability induced by APP (Table I), it can be inferred that the cleavage of the polymer chain occurs at lower temperature through the protonation of the urethane linkage according to Scheme II.

Polymer IX. Figure 7a shows the mass spectrum of polyurethane IX recorded at a probe temperature of 460 °C. The inspection of the spectrum reveals the presence of two molecular ions at *m/z* 228 and 594 corresponding to oligomers of structure



This implies that the pyrolytic breakdown of polyurethane IX occurs by transfer of a hydrogen atom from the α-methylene group of the piperazine ring to the oxygen atom, as illustrated in eq 8, with formation of compounds having phenolic end groups.

 (8)

Due to the high PDT of this polymer, the 4,4′-isopropylidenediphenol unit undergoes thermal disproportionation (eq 5), as indicated by the high intensity of peaks at *m/z* 94 and 134 in the spectrum in Figure 7a. All other peaks detected in the spectrum have been identified as EI fragments of compounds above reported.

The mass spectrum detected for the polymer IX–APP mixture, Figure 7b, is nearly identical with that of the pure polymer.

Considering the reduction of thermal stability caused by APP (Table I), one can deduce that the protonation of the urethane linkage induced by APP catalyzes the cleavage of polyurethane chain.

Conclusions

The thermal degradation pathways of polyurethanes (Table I) appear to be strongly influenced by structural factors. The presence of APP affects the thermal decomposition in several ways, lowering the thermal stability in polyurethanes having a PDT value higher than 370 °C and changing often the nature of the pyrolytic products formed.

In the polymers I and VI the data indicate that APP is inducing a hydrolytic cleavage on the polymer chain. In the case of polymer IV, the addition of APP enhances the formation of tertiary amines through protonation of the urethane nitrogen (Scheme I). In the other cases (polymers V and VII), protonation of the nitrogen atom catalyzes selectively some thermal decomposition pathways.

The principal mechanisms of thermal fragmentation ascertained by studying the polyurethanes in Table I are summarized in Scheme IV. Three thermal degradation

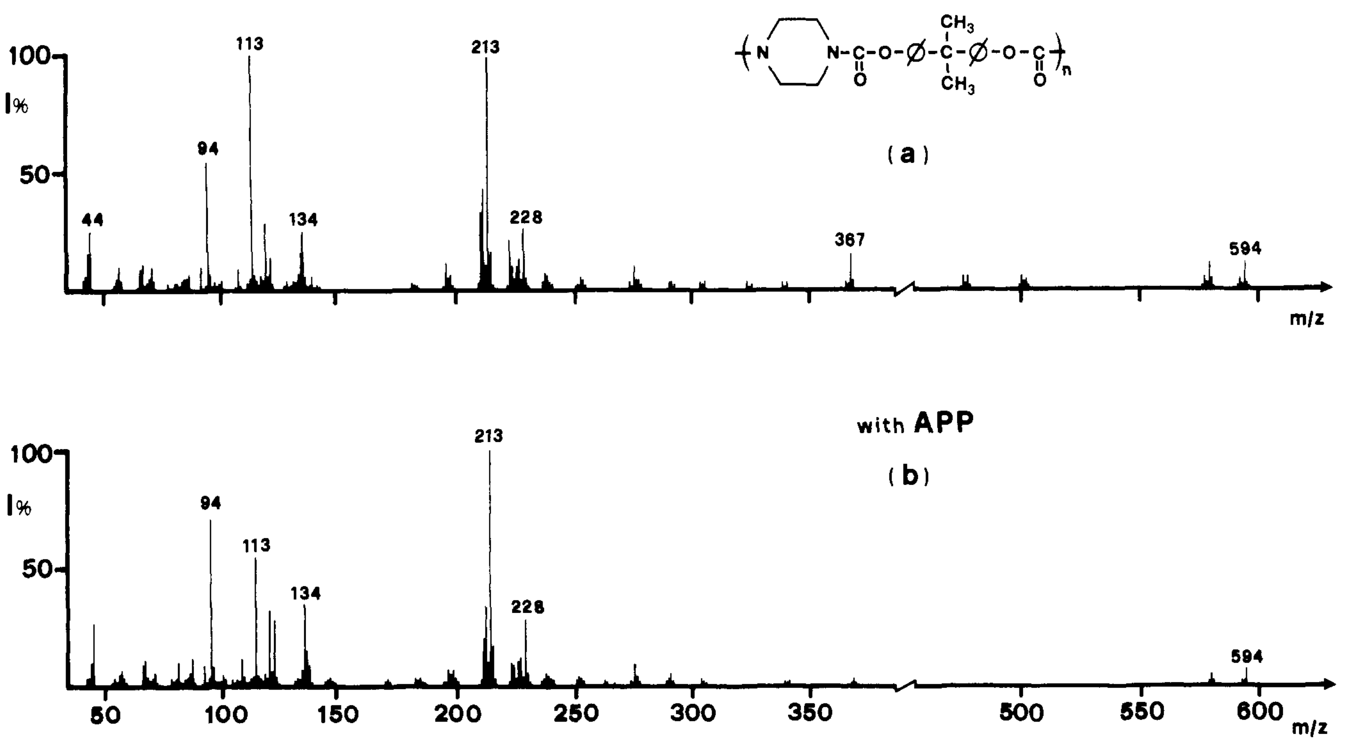
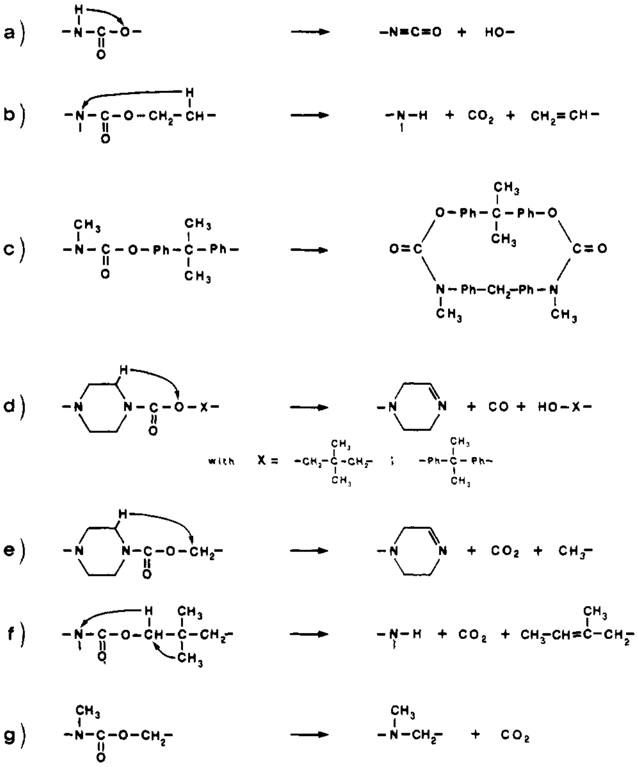


Figure 7. Mass spectra (18 eV) of the thermal degradation products of (a) polyurethane IX at a probe temperature of 460 °C and (b) polyurethane IX–APP (10%) mixture at 430 °C.

Scheme IV



pathways are occurring: N–H hydrogen transfer (polymers I–III; Scheme IVa), β-CH hydrogen transfer (polymers IV and VII; Scheme IVb), and α-CH hydrogen transfer (polymers V, VI, VIII, and IX; Scheme IVd–f). As a consequence of the different energy requirements of these three processes, the thermal stability of polyurethanes increases going from N–H to N-substituted polyurethanes. Among the latter, it is higher for polymers V, VI, VIII, and IX with respect to IV and VII (Table I).

Thermal degradation processes occurring in N-substituted polyurethanes (IV–IX) involve, as a rate-determining step, either an α- or a β-CH hydrogen transfer to the nitrogen or oxygen atoms (Scheme IV).

The α-CH hydrogen transfer occurs at relatively high temperatures (about 480 °C, Table I). Therefore, protonation of the urethane nitrogen atom by acid species generated through the APP decomposition causes a decrease of the thermal stability of polymers V, VI, VIII, and IX (Table I), since it catalyzes the α-CH hydrogen-transfer process.

In contrast, the thermal stability of polymers IV and VII is unaffected by APP. In these cases, the β-CH hydrogen-transfer process occurs at relatively low temperatures (about 380 °C, Table I). The protonation of the urethane nitrogen induced by APP causes a change in the pyrolytic products, but the overall energy requirement for the thermal degradation remains nearly unaffected.

In the case of the N–H polyurethanes, the N–H hydrogen-transfer process occurs at temperatures even lower (about 300 °C, Table I), with respect to N-substituted polyurethanes, so that the thermal effect of APP on the PDT (Table I) is nearly negligible even when it induces hydrolytic cleavage.

Acknowledgment. This work was carried out under Contract 82.00647.95 (Consiglio Nazionale Richerche (Rome), Finalized Project on Fine and Secondary Chemistry).

References and Notes

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(2) S. Foti, M. Giuffrida, P. Maravigna, and G. Montaudo, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1201 (1984).
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Syntheses and Characterization of Heteroatom-Bridged Metal-Free Phthalocyanine Network Polymers and Model Compounds

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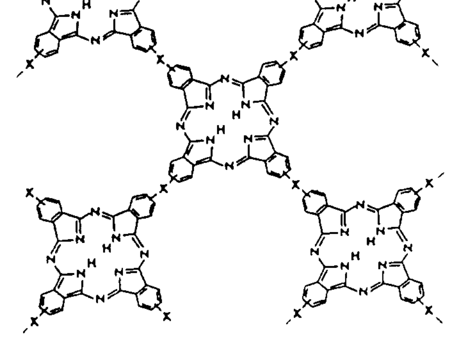
ABSTRACT: Procedures for the preparation of metal-free phthalocyanine network polymers from oxygen-, sulfur-, and selenium-bridged bis(phthalonitrile) monomers were investigated on the basis of phthalocyanine model compounds derived from phenoxy-, (phenylthio)-, and (phenylseleno)phthalonitrile compounds. The oxygen- and sulfur-substituted phthalonitrile compounds could be converted in high yield to the corresponding metal-free phthalocyanine compounds by reaction with tetrahydropyridine, hydroquinone, or 4,4′-biphenol. With an optimum quantity of coreactant, the phthalocyanine yield ranged from near-quantitative to 65% to no conversion for the respective oxygen, sulfur, and selenium phthalonitriles. A side reaction to a triazine structure was also investigated. The model phthalocyanine compounds were characterized by IR, electronic, ^{1}H NMR, and X-ray diffraction spectroscopies and TGA, from which an analysis of the corresponding phthalocyanine network polymers was made. Spectroscopic analysis and sulfuric acid insolubility indicated a significantly higher phthalocyanine content in the oxygen-bridged network polymer. Both phthalocyanine model compounds and network polymers had very high electrical resistivities, and the polymers were not dopable with iodine.

Introduction

As a polymer-forming reaction, the cyclotetramerization of a phthalonitrile functional group to a phthalocyanine macrocycle presents a route where, ideally, a bis(phthalonitrile) monomer is transformed to a phthalocyanine network polymer. Energetically, the high aromatic character of the phthalocyanine ring[1] makes this reaction very favorable. This polymerization was first studied by Marvel and Martin, who used 3,3′,4,4′-tetracyanodiphenyl ether in a heterogeneous fusion reaction with copper bronze at 275 °C.[2] Numerous subsequent polymerizations of bis(phthalonitriles) under fusion reaction conditions with metals or metal salts have been reported[3] although structural characterization of the products has been lacking. Marvel and Martin initially cautioned that the polymerization progresses beyond the dimer and trimer stage only with difficulty. Boston and Bailar have demonstrated by careful model compound work that a 1,2,4,5-tetracyanobenzene–cupric chloride polymerization does not progress beyond the formation of monomeric phthalocyanine complexes.[4] While these reaction conditions have been developed by Linstead and co-workers for conversion of simple phthalonitrile to phthalocyanine compounds,[5] an incomplete molecular dispersal of the metal or metal salt coreactant in a network-forming organic polymer system can set a limit on the degree of conversion obtainable. This coreactant dispersion problem may be circumvented by use of a compatible soluble organic coreactant for conversion of the phthalonitrile to the metal-free phthalocyanine. The patent literature, while lacking analytical characterization, contains claims of several examples of such reagents, which include alcohols, amines, and amides.[6] We have recently found that metal-free phthalocyanine compounds can be prepared in high yield from phthalonitriles in the presence of an appropriate proton-donating organic reducing agent such as hydroquinone and that such coreactants are very useful for curing bis(phthalonitrile) monomers to phthalocyanine resins.[7]

In the present work the objective is to prepare phthalocyanine network polymers from heteroatom (oxygen, sulfur, and selenium) bridged bis(phthalonitrile) monomer melts (eq 1) and to investigate their potential as electrically



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