Mass Spectrometric Detection of Cyclic Oligomers in Polyurethanes and Polyureas

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ABSTRACT: The synthesis and characterization of four novel cyclic oligomers (I–IV) formed in some polycondensation reactions leading to polyurethanes and polyureas are reported. Simultaneous detection and identification of these compounds directly from the polycondensation mixtures have been achieved by mass spectrometry (MS). The four cyclic oligomers, subsequent to detection by MS, have been isolated by solvent extraction and characterized. Details of the MS method used are given, and its potential is discussed.

Introduction

The production of high molecular weight polymers is often accompanied by the formation of sizeable amounts of cyclic oligomers.[1-3] Among the various classes of macromolecular compounds, polycondensates are the most rich in oligomers.[1-3]

We have been interested in the synthesis and characterization of a series of polyurethanes[4,5] and polyureas[6] and have found several cases in which cyclic oligomers were formed in the polymerization reactions.

Current methods for detecting low amounts of oligomers contained in polymeric samples are based almost exclusively on gas–liquid and gel permeation chromatography.[2,7] These separation techniques are indeed powerful, but sometimes low volatility of samples or low solubility in most organic solvents makes alternative and rapid methods of detection and identification for low molecular weight compounds desirable. Mass spectrometry (MS) is particularly suitable to detection of these materials since they are volatile under high vacuum at relatively mild temperatures, while polymers remain undecomposed.[8-10]

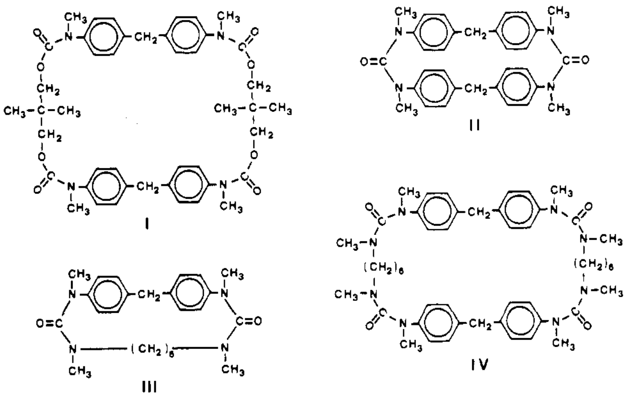
Here we have used MS to detect and identify, without previous isolation, one cyclic urethane (I) and three cyclic ureas (II–IV) (Chart I) formed during three dispersion polycondensation reactions leading to polymers of the corresponding structure. Since these oligomers are unreported, they were subsequently isolated from the polymer and characterized by NMR spectrometry and MS.

Experimental Section

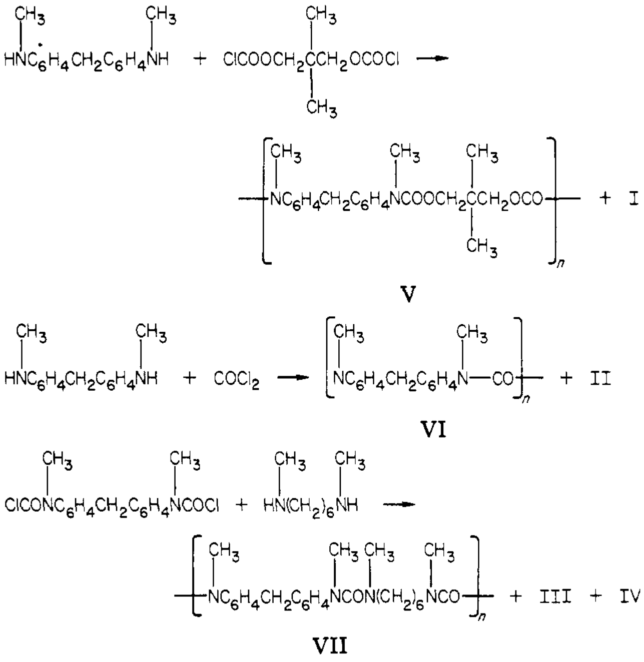
Materials. 4,4′-Methylenebis[*N*-methylaniline] was prepared by the method of Fedotova et al.[11] 4,4′-Methylenebis[*N*-methylcarbaniloyl chloride] was prepared by reacting in toluene 4,4′-methylenebis[*N*-methylaniline] and an equimolar amount of *N,N*-dimethylaniline as an acceptor of HCl with an excess of $COCl_2$ in toluene at room temperature for 3–4 h. The hydrochloride of *N,N*-dimethylaniline was filtered, the solution distilled at reduced pressure, and the residue recrystallized from ligroin; mp 98–100 °C. The bis(chloroformate) of 2,2-dimethyl-1,3-propanediol was analogously prepared; bp 85–86 °C (0.5 mm). Other starting materials were commercial products, appropriately purified before use.

Polymers. The polyurethane and the polyureas corresponding to oligomers I–III were prepared by dispersion polycondensation, starting from the amine and from the chloroformate of the *N*-methylcarbaniloyl chloride as shown in Scheme I. A typical procedure (polymer VII) was as follows: In a Waring blender were placed 1.44 g (0.01 mol) of 1,6-bis(methylamino)hexane, 2.24 g (0.02 mol) of Na_2CO_3, and 0.35 g of sodium lauryl sulfate in 35 mL of water. To the rapidly stirred system was added all at once 3.51 g (0.01 mol) of 4,4′-methylenebis[*N*-methylcarbaniloyl chloride] in 40 mL of tetrahydrofuran.

Chart I



Scheme I



The mixture was stirred for 5 min and then poured into 500 mL of water. Tetrahydrofuran was removed by gentle warming under vacuum, and the polymer that precipitated was filtered, washed with water, and dried in vacuo at 50 °C. The crude polymer was dissolved in DMF and the solution was filtered through a medium-porosity sintered-glass funnel and slowly dropped into distilled water. After standing overnight, the polymer was filtered and dried in vacuo at 50 °C; yields of crude polymers, 75–90%.

Viscometry. Inherent viscosities ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) of the polymers were measured in DMF in a Desreux-Bishoff suspended level viscometer; the temperature was maintained at 30.00 ± 0.01 °C. The viscosities and melting points were as follows: V, $\eta_{inh} = 0.38$ dL/g, mp 170–190 °C; VI, $\eta_{inh} = 0.15$ dL/g, mp 250–280 °C; VII, $\eta_{inh} = 0.14$ dL/g, mp 110–180 °C.

Cyclic Oligomers. Polymers were dissolved or extracted with the appropriate solvent; the oligomers were collected as insoluble products or by concentrating the solvent, recrystallized, and characterized by MS and ^1H NMR spectrometry (Table I).

Table I
Isolation and ^{1}H NMR Characterization of Oligomers I-IV

				^{1}H NMR data (δ)						
compound	solvent	mp, °C	oligomer, %[c]	Ar[d]	$ArCH_2Ar$[e]	CH_2O[e]	$N(Ar)CH_3$[e]	N(R)-CH_3[e]	$N(CH_2)_6N$[f]	CCH_3[e]
I	acetone[a]	254-255	3	7.17	3.97	3.77	3.30			0.78
II	MeOH[b]	300-301	4	6.78	3.80		3.23			
III	MeOH-THF[b]	157-158	5	7.21	3.87		3.17	2.70	0.25-1.26	
IV	MeOH-THF[b]	180-181	2	7.13	3.96		3.20	2.63	0.93-1.70	

[a] Extraction. [b] Dissolution. [c] Weight percent of oligomer in the polymer. [d] Quartet. [e] Singlet. [f] Multiplet.

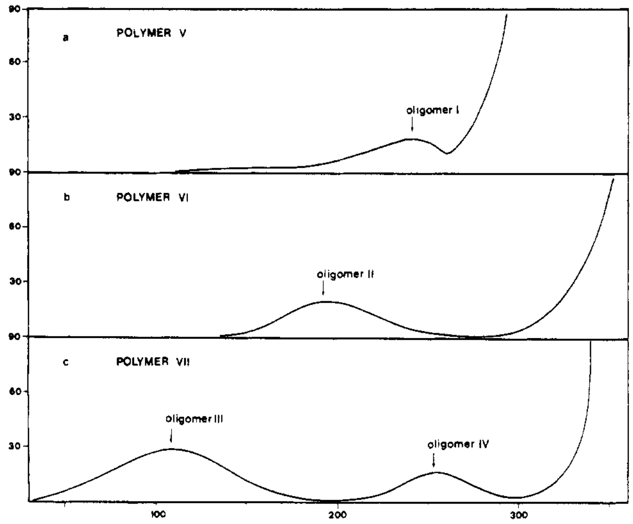


Figure 1. Total ion current (TIC) vs. temperature curves for polymers V (a), VI (b), and VII (c).

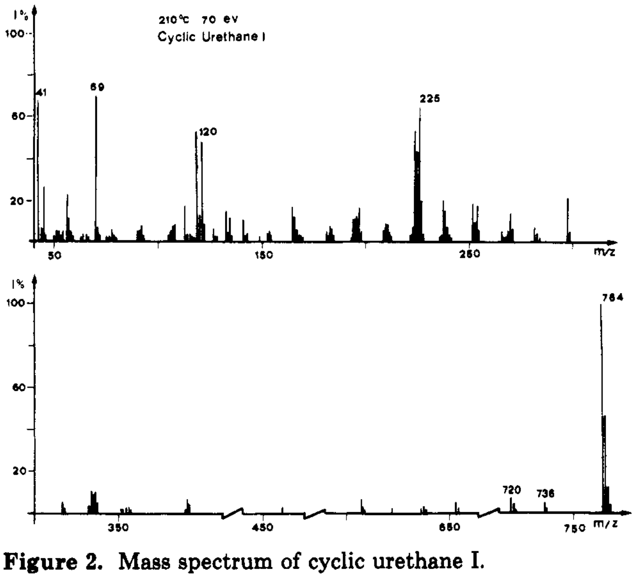


Figure 2. Mass spectrum of cyclic urethane I.

Mass Spectrometry. Polymer samples were introduced by using the direct-insertion inlet for solid samples of an LKB-9000S electron impact mass spectrometer. The probe was heated at 10 °C/min up to 360 °C. During the heating program, the total ion current (TIC) was collected and repetitive mass scans were performed. Details of the experimental procedure are described elsewhere.[8]

Results and Discussion

Mass spectrometric detection of oligomers contained in our polymers has been achieved by directly introducing the polycondensation mixtures into the ion source of a MS by the conventional direct-insertion rod for solid samples. The probe temperature is then gradually increased on a linear program, and the evolving products are analyzed by repetitive mass scans. Using this method, it is possible to select the heating program which permits the best time–temperature resolution of the mixtures (a heating rate of 10 °C/min was found to be adequate in the present case).

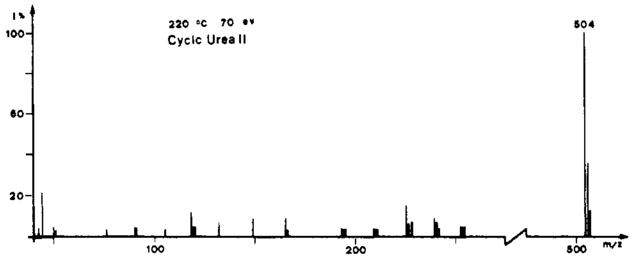


Figure 3. Mass spectrum of cyclic urea II.

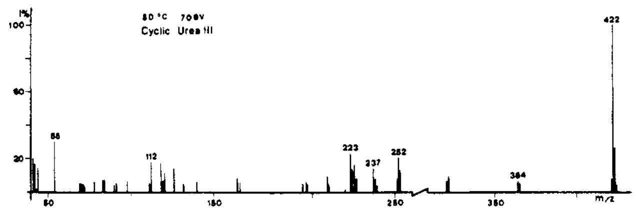


Figure 4. Mass spectrum of cyclic urea III.

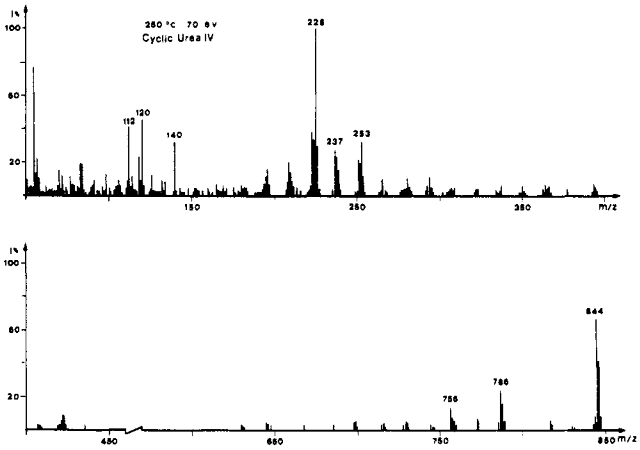


Figure 5. Mass spectrum of cyclic urea IV.

Cyclic oligomers, which evaporate undecomposed in the high vacuum of the ion source, are usually detected as separate peaks in the total ion current (TIC) curves before the evolution of the thermal decomposition products originating from the polymer pyrolysis.

Figure 1 reports the TIC vs. temperature curves for the three polycondensates analyzed here. These curves somehow resemble chromatographic tracings and, actually, each peak corresponds to the evolution of a cyclic oligomer. Figure 1c shows the remarkable resolution of oligomers III and IV achieved by the gradual heating procedure. The evolving products are analyzed by repetitive mass scans, so that each TIC peak can be directly identified through its mass spectrum.

Figures 2–5 show the mass spectra corresponding to the four cyclic oligomers detected. The four mass spectra show intense peaks at high masses which correspond in all cases to the molecular ion of the compound. This feature is characteristic of mass spectra of cyclic compounds and therefore permits an easy detection of these compounds by MS. Further peaks in the spectrum of oligomer I (Figure 2) originate from loss of CO (peak at m/z 736) and CO_2 (peak at m/z 720) from the molecular ion. A metastable peak corresponding to the latter fragmentation is found in the spectrum.

Cyclic urea II (Figure 3) is very stable to electron impact and the molecular ion is by far the most intense peak observed.

Compound III (Figure 4) shows loss of hydrogen from the molecular ion and loss of a neutral fragment of mass 57 from the molecular ion and from the M - 1 peak (ions at m/z 365 and 364, respectively). The neutral fragment lost probably corresponds to CH_3NCO. The same fragmentation pattern gives the peaks at m/z 787 and 786 in compound IV.

Loss of methyl isocyanate is an EI process similar to the very frequent loss of CO_2 observed in the EI spectra of cyclic esters, carbonates, and urethanes.[6,9,10]

As mentioned above, since the cyclic oligomers identified here are novel compounds, after their detection in the polycondensation mixtures, they were isolated from the polymers by solvent extraction and subsequent crystallization. The mass spectra of the pure compounds were identical with those shown in Figures 2-5, and the ^1H NMR spectra were in agreement with formulas I-IV (Table I).

Conclusion

The foregoing examples show the remarkable potential of MS in the detection of cyclic oligomers contained in polymeric samples. The unique advantage of this method consists in allowing simultaneous detection and identification of the cyclic oligomer, therefore eliminating the isolation and subsequent identification steps.

Furthermore, we have observed that when a linear programmed heating of the probe is used, the "retention times" of the cyclic oligomers (i.e., the peak appearance in the TIC curves) are quite constant.

This encourages further development of the MS method to the detection and separation of more complex oligomer mixtures. In the latter case, the use of single-ion curves (SIC),[8] corresponding to the intensity of a single mass ion, might prove very useful for increasing the "resolution" of this technique.

Acknowledgment. This work was partially supported by Consiglio Nazionale delle Ricerche (CNR), Rome.

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Gas Chromatographic Investigation of Poly(vinylidene fluoride)-Poly(methyl methacrylate) Blends

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ABSTRACT: Inverse gas chromatography was used to investigate the thermodynamic miscibility of molten poly(vinylidene fluoride)-poly(methyl methacrylate) blends. In addition to glass transition and melting point depression data, polymer-polymer interaction parameters, χ_{23}', were determined from the measured retention data for various polar and nonpolar probes in pure and mixed stationary phases of these polymers. Negative interaction parameters are observed in accordance with the well-known miscibility of these blends. The magnitude and the trend in the composition dependence of χ_{23}' are in excellent agreement with literature results obtained from small-angle X-ray scattering and calorimetry.

Introduction

There is currently a great deal of research interest in miscible polymer blends since such mixtures may represent a valuable and economical alternative to the use of copolymers.[3,4] However, truly miscible multicomponent polymer systems are rather infrequent. A thermodynamic study of polymer-polymer interactions can lead to an understanding of the resulting blend's miscibility and therefore to the selection of compatible polymer systems.

Recently, the usefulness of inverse gas chromatography (IGC) in the investigation of polymer-probe and polymer-polymer interactions has been widely recognized.[3,5] This method provides a fast and convenient way of obtaining thermodynamic data for concentrated polymer systems.

Mixtures of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVF_2) have recently been the subject of great interest. A number of workers have reported evidence of true molecular mixing of these two polymers over a wide range of composition.[6-9] Calorimetric measurements and various spectroscopic techniques, including X-ray scattering,[7] Fourier transform infrared

0024-9297/82/2215-0885$01.25/0