

PRODUCTION AND THERMAL DECOMPOSITION OF POLYCONDENSATES CONTAINING N,N'-DISUBSTITUTED THIOUREA DERIVATIVES

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Polycondensates containing N,N'-ethylenethiourea or N,N'-diisopropylthiourea units and titanium or silicon-derived coupling agent molecules were prepared. Their structures were confirmed through FTIR spectroscopy. The thermal decomposition of these polycondensates was studied by means of TG and DTA methods and FTIR and ESR spectroscopy.

Introduction

Several techniques, including the addition of stabilizers and crosslinking, have been employed to improve the thermal stability of polymers [1, 2]. It has been established that the presence of nitrogen in a polymer generally leads to an improved thermal stability [3, 4]. It has also been shown that the use of titanium and silicon-derived coupling agents as molecular bridges between the interface of an inorganic surface and an organic polymer matrix leads to the increased flame resistance of composites [4-7].

The complex polycondensation formation of urea-formaldehyde-N,N'-disubstituted thiourea derivatives with a coupling agent is described in this paper. The structures of these polycondensates were confirmed through Fourier transform infrared (FTIR) spectroscopy. Their thermal decomposition was investigated by means of thermogravimetry (TG), differential thermal analysis (DTA) and FTIR spectroscopy. In addition, as the thermal decomposition of polymers is generally considered to a free radical process [8], we also report electron spin resonance (ESR) studies on the free radical produced during thermal treatment of the polycondensates in question.

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Experimental

Preparation

A mixture of 1.2×10^{-1} moles of 35% formaldehyde and 1.0×10^{-1} moles of urea (*pH* 7.5–8) was added to 1.5×10^{-2} moles of N,N'-ethylenethiourea and 9.1×10^{-2} moles of silicon(IV) oxide (1) or 1.5×10^{-2} moles of N,N'-diisopropylthiourea and 9.1×10^{-2} moles of titanium(IV) oxide (2). These mixtures were stirred at 353 K for 2.4×10^3 s. After this period, the *pH* was adjusted to 5 through addition of an acid catalyst and the mixtures were stirred at 363 K for 3.6×10^3 s. After adjustment to *pH* 7.5, the mixtures were cooled to 298 K. The polycondensates were filtered off and dried at 373 K.

Fourier transform infrared spectroscopy

The FTIR spectra of the polycondensates were recorded with a Perkin Elmer 1600 FTIR spectrophotometer, using the KBr pellet (1 mg/150 mg KBr) technique. The samples were also heated at a desired temperature from 493 K to 773 K for 1.2×10^3 s, and then cooled to room temperature, and their FTIR spectra were examined to study the chemical changes during heating.

Thermogravimetry and differential thermal analysis

TG and DTA curves were recorded on a Du Pont 951 thermogravimetric analyzer and 407 Netzsch derivatograph in a dynamic atmosphere of pure air. Thermal analyses were performed under the following conditions: polycondensates were heated in the temperature range 293–1273 K, at a heating rate of $10 \text{ deg} \cdot \text{min}^{-1}$; the reference substance was Al_2O_3 .

Electron spin resonance spectra

Polycondensates in the pure solid state were pyrolyzed by heating to the desired temperature from 493 K to 873 K for 1.2×10^3 s in air. The ESR spectra were recorded on a Bruker 200 D ESR spectrometer at 100 kHz modulation and a nominal frequency of 9.5 GHz. Linewidths were measured from first derivative curves (peak-to-peak). Signal intensities (proportional to the spin concentrations) were calculated by double integration of the first derivative spectrum. These two ESR parameters were measured at room temperature.

Results and discussion

The combination of urea and formaldehyde begins with a series of addition reactions, followed by the condensation of methylol groups in methylol bridges to form methylene ether bridges at higher temperature [8–10]. However, the mechanism of a reaction system such as urea-formaldehyde- N,N' -ethylenethiourea-silicon(IV) oxide (1) or urea-formaldehyde- N,N' -diisopropylthiourea-titanium(IV) oxide (2) involves a series of complex polycondensation processes. In this way, the polycondensates contain less formaldehyde and ecological problems in the application step are reduced. The products were characterized by means of FTIR spectroscopy (Table 1).

Table 1 FTIR spectral data of polycondensates 1 and 2 (frequency / cm^{-1})

Assignment of band	1	2
$\nu(\text{NH})$	3305 (s)	3300 (s)
$\nu(\text{CH})$	2970 (w)	2965 (w)
$\nu(\text{CO}) + \delta(\text{NH}) + \nu(\text{CN})$	1640 (s)	1635 (s)
	1562 (s)	1560 (s)
$\delta(\text{CH})$	1438 (w)	1437 (w)
$\nu(\text{SCN})$	1380 (m)	1375 (m)
$\nu(\text{CN})$	1255 (m)	1250 (m)
$\tau(\text{NH}) + \rho(\text{NH}) + \varphi(\text{CH}) + \varphi(\text{CN})$	1140 (m)	1130 (m)
	1040 (m)	1044 (m)
	810 (w)	810 (w)
	680 (m)	662 (w)
	550 (m)	550 (m)

s = strong, m = medium, w = weak

In order to study the physicochemical changes that occur during thermal treatment, the variations in the FTIR spectra of the polycondensates at various temperatures were studied. To record the effect of temperature on the IR absorption bands, the samples were kept at 493, 533, 573, 623, 673, 723 and 773 K for 1.2×10^3 s. It is seen that the intensities of functional group IR bands (Table 1) of samples at 3300 or 3305 cm^{-1} (νNH), 1635 or 1640 cm^{-1} and 1560 or 1562 cm^{-1} (νNHCO , amide I and II), 1437 or 1438 cm^{-1} (δCH), 1375 or 1370 cm^{-1} (νSCN), 1250 or 1255 cm^{-1} (νCN) and 1130 or 1140 cm^{-1} ($\nu\text{NCH}_2\text{O}$) are decreased on heating, and they disappear at about 573 K. At higher temperatures, above 773 K, aromatic ring bands appear [7].

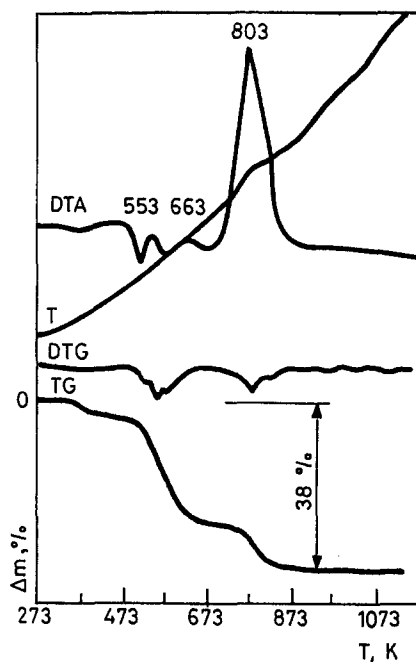


Fig. 1 TG-DTG-DTA traces of polycondensate 1

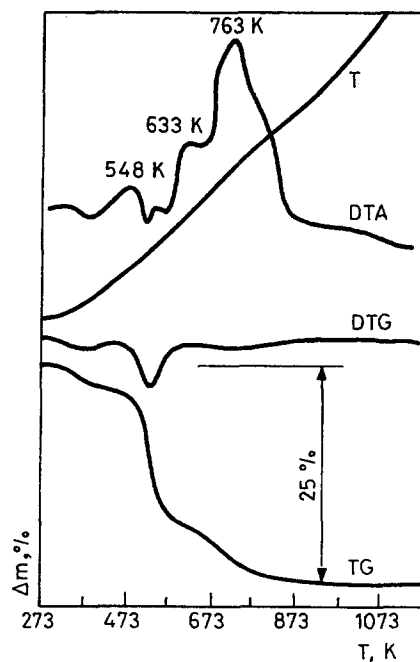


Fig. 2 TG-DTG-DTA traces of polycondensate 2

Figures 1 and 2 illustrate TG-DTG-DTA curves of polycondensates 1 and 2 obtained under a dynamic heating program:

The thermal analyses (Table 2) show that the thermal decompositions of samples 1 and 2 occur in several reaction stages of weight loss of different natures, followed by exo- and endothermic effects. In each stage partial volatilization occurs, while the polycondensates undergo chemical modification. The thermoanalytical data indicate that the second stages involve a major weight loss (20.5 and 12%) with indistinct separation, and that the temperature of the main exothermic decomposition process is 533 K for sample 1 and 523 K for sample 2 [11, 12].

Table 2 TG, DTG and DTA reaction stages of polycondensates 1 and 2

Thermal reaction stage	1	2
First		
Temperature range, K	303 – 498	303 – 493
Weight loss, %	4.5	4.3
DTA peak, K	363 (endo)	378 (endo)
Second		
Temperature range, K	498 – 583	493 – 563
Weight loss, %	20.5	12
DTA peak, K	533 (exo)	523 (exo)
Third		
Temperature range, K	583 – 743	563 – 833
Weight loss, %	3.5	8.7
DTA peak, K	663 (exo)	633 (exo)
Fourth		
Temperature range, K	743 – 823	
Weight loss, %	9	
DTA peak, K	803 (exo)	

On the basis of the results of the thermal analyses, supported by the FTIR spectral data, it is proposed that polycondensate 1, prepared with N,N'-ethylenethiourea as the component for the thermostabilizing effect and silicon(IV) oxide as the coupling agent, has a better thermal stability than that of polycondensate 2, prepared from N,N'-diisopropylthiourea and titanium(IV) oxide.

ESR analyses indicate that stable free radicals appear above 523 K. Figure 3 depicts the changes in concentrations of free radicals (relative ESR signal intensities, N) of the pyrolyzed polycondensates as a function of

temperature. In the temperature range from 523 to 873 K, the relative ESR signal intensities increase with increasing temperature up to about 823 K.

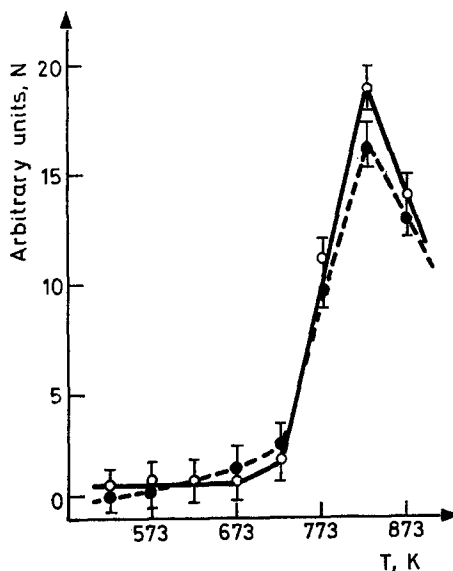


Fig. 3 Variations of normalized ESR intensities, N (in arbitrary units) vs. T , K: The polycondensate 1 free radicals (—) and the polycondensate 2 free radicals (- - -)

The decrease in the ESR linewidths with increasing temperature (Fig. 4) shows that conjugation is being extended between the chains [13]. The ESR

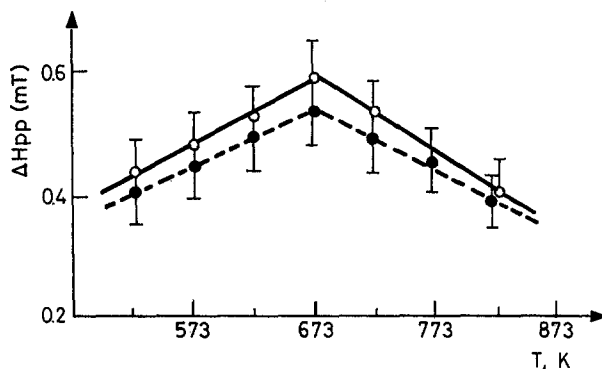


Fig. 4 Variation of the ESR linewidths, ΔH_{pp} (mT) vs. T , K: The polycondensate 1 free radicals (—) and the polycondensate 2 free radical (- - -)

study indicated that at higher temperature the intermolecular condensation reactions in the synthesized polycondensates proceed by a free radical mechanism.

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Zusammenfassung — Es wurden Polykondensate mit einem Gehalt an N,N'-Ethylthiokarbamid- oder N,N'-Diisopropylthiokarbamideinheiten und mit Titan oder Silizium abgeleiteten Koppelreagenzmolekülen hergestellt. Ihre Struktur wurde mittels FTIR Spektroskopie bestätigt. Die thermische Zersetzung dieser Polykondensate wurde mittels TG und DTA Verfahren sowie mit Hilfe von FTIR und ESR Spektroskopie untersucht.