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Thermogravimetric Study of Polyisothiocyanato-Styrenes

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Polyisothiocyanato-styrene (PITCS) was prepared by radical polymerization corresponding monomers. The polymers were characterized by physical and spectral studies. The polymer showed excellent stability. Their inherent viscosities were in the range of 0.26-0.32 dL/g. Thermal study of the polymers, poly-2, poly-3, poly-4-isothio-cyanato-styrene, poly-2,4-diisothiocyanato-styrene and 4-isothio-cyanato-styrene oligomer show, the increase of temperature till 230°C. After that they transform into three dimensional structure without the weight loss. However, because of this structure the weight decreases slowly and their destruction temperature exceeds that of the polystyrene by a temperature varying from 220-230°C. The weight loss speed is tightly linked to the 4-isothiocyanato-styrene oligomer.

Key Words: Thermogravimetric, Polystyrene, Thermal stability, Cross-linking, Isothiocyanato-styrene.

INTRODUCTION

The temperature of rapid weight loss of polystyrene in a temperature ramped thermal gravimetric experiment in air, which is 270°C for the unstabilized polymer, can be raised to 305 and 320°C when 1% C 60/C 70 Fullerenes and C 70, respectively, are added[1]. It is known that the compound containing trimellitimide acid and urazole moieties, by polymerization reaction, gave novel polyureas polymer and that the presence of these functional groups will make these polymers such as polyureas cross-linkable[2].

However, polystyrene are generally known which offer little resistance to heat and causes the disappearance of their properties from 100 to 120°C, which limits relatively their technical applicability. Thus, thermal stability of polystyrene has received extensive attention. One accepted approach for the improvement of thermal stability of polystyrene is the chemical

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modification of their structure by introducing functional groups into the aromatic cycle.

Many works[3,4] have been carried out and showed the effect of the functional groups on the thermal stability of polymers, *e.g.* Tamami *et al.*[5] concluded that the aliphatic polyureas started to loss weight, because of thermal degradation, around 230°C and for aromatic polyureas this temperature was around 390°C. The 5 % weight loss of the polymers was in the range of 245-420°C. More attention has been paid to modify the polyurethane by heterocyclic groups such as isocyanurate[5-7], oxazolidone[8-10] and imide[11-13] groups into the backbone of polyurethane.

The polymers containing -NCS groups offer a high chemical reactivity. In the softness conditions and in different chemical reactions, the coloured polymers having stabilized structures react easily with the acetones, aldehydes, *etc.*[14].

In this work, the purpose is to investigate the influence of the -NCS group positions in the monomer unit, on the thermal stability of polymers. Thermogravimetric analysis of poly-2-, poly-3-, poly-4-isothiocyanato-styrene (PITCS), poly-2,4-diisothiocyanato-styrene (PDITCS) and the oligomers of 4-isothiocyanato-styrene (O-4-ITCS) are reported herein.

EXPERIMENTAL

All chemicals were purchased from Aldrich and used after purification. Inherent viscosities ($\eta_{inh.} = \ln\eta_T/c$ at a polymer concentration of 0.5 g/dL) were determined for a solution of 0.5 g/dL in cyclohexanone as solvent at 30°C using an Ostwald viscosmeter.

IR spectra were recorded on Shimadzu 435 IR spectrophotometer using KBr pellets. The infrared spectra of the samples dispersed in dry KBr pellets were recorded between 4000-400 cm^{-1}. Chemical processes which take place in the chain of heated polymers at 200-230°C during 3 h, are followed by FT-IR. Differential thermal (DTA) and thermogravimetric analysis (TGA) measurement were performed in the temperature range, 20-800°C on Shimadzu DTA-50 and TGA-50 thermal analyzers, respectively. The heating rate of 5°C/min in air for DTA and 5°C/min under nitrogen atmoshphere for TGA are performed.

Shimadzu GC-9A gas chromatography equipped with a flame ionization detector (FID) linked to a data processor (Shimadzu C-R6A) capable of plotting a chromatogram and printing data on the same recording thermal chart paper was used for the chromatographic analysis of pyrolytic products obtained in the range of temperature 340-410°C.

Polymer synthesis: The mixture of 5×10^{-2} mol of monomer 2-, 3- and 4-isothiocyanato-styrene[15], cyclohexanone (2mL) and bisisobutyronitrile (AIBN), was used as initiator ([I] = 2 mol %) after the elimination of air from reaction area, the pyrex glass ampoules sealed off under high vacuum. The sealed ampoules were immersed in a water bath held at the required temperature of polymerization 80°C. After the desired time (6 h), the ampoules were removed from the bath and the mixture was poured into a large amount appropriate non-solvent (*n*-hexane). The precipitated polymer was collected and dried in vacuum at 50°C for 1 h till the stabilization of its weight occured.

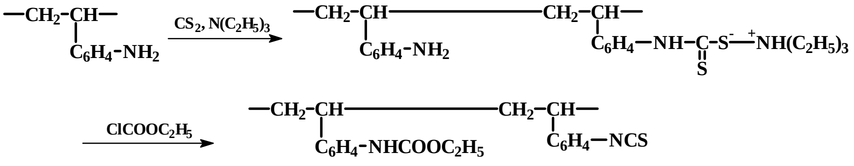
Oligomer synthesis: Oligomer prepared[15] from oligomer 4-aminostyrene (degree of polydispersity n = 30) by the action of CS_2 and the triethylamine with the reduction of dithiocarbamate salt by the ethylchloroformate as the habitual components[16].

The IR spectra of synthesized PITCS and PDITCS shows stretching vibrations of aliphatic (C-H) at 2967-2909 cm^{-1} and aromatic (C-H) at 3060 cm^{-1}, aromatic (C=C) at 1491 cm^{-1}, stretching vibration band (characteristic peak) of (N=C=S) at 2000-2250 cm^{-1} (strong), stretching vibration of (C=S) at 1225-1190 cm^{-1}, stretching vibration of aliphatic $-CH_2$ peak at 1448 and 1108 cm^{-1} (C-N stretching). Yield of the polymers (1-4) *ca.* 95 %. Elemental analysis (%): Found for C_9H_7NS, C 67.64, H 5.17, N 7.26, S 19.87, Calcd. C 67.08, H 4.34, N 8.69, S 19.87.

The elemental analysis results for PITCS and PDITCS are in good agreement with the structure of polymers and calculated percentages for carbon, hydrogen, nitrogen, sulphur contents in polymer repeating unit of PITCS.

RESULTS AND DISCUSSION

Oligomer O-4-ITCS has been obtained by scheme:

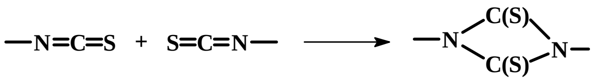


The decreasing value of sulphur in composition suggest that only a quantity of 60 % of amino groups ($-NH_2$) is transformed into isothiocyanate (-NCS), one part is transformed into carbamate groups, which could be easily identified by infrared spectroscopy [ν(N-H), 3400 cm^{-1}, ν(C=O), 1740 cm^{-1}].

The complete thermogravimetric analysis data showed that the insertion of isothiocyanate functional groups within the macromolecule of polystyrene leads to the raising of its total destruction temperature around 230°C.

The increase of the thermal stability of these polymers by comparing with the polystyrene finds its explanation by the participation of -NCS groups in the reconstruction process of the macromolecule. The process of thermolysis involved two stages.

The first stage (temperature till 230°C) is executed without thermal effects and without weight loss for all polymers except for the oligomer. At this stage the macromolecule reticules (cross-linked), apparently according to the following reaction:



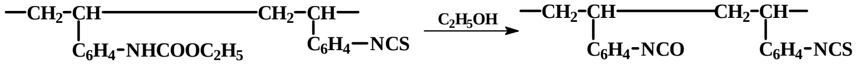
In accordance with Yeganeh *et al.*[17], the temperature stability of polymers raising is due to the strong dipole-dipole interaction of imide groups present in the polymers backbone which are responsible for improvement of thermal properties.

It is noted that the process starts around 150°C. The films heated at this temperature during 3 h, lose their solubility, but perfectly blow up in the organic solvents such as cyclohexanone or chloroform. The films heated at 200°C hardly blow up. There is no weight loss in the vicinity of 200°C of the films, thus P-4-ITCS showed a diminishing of the characteristic stretching absorption band of -NCS groups, 2200-2000 cm^{-1} of about 10 % comparing to the spectra of polymer without or thermal treatment.

At the temperature 240°C and during 3 h, the polymers acquired many chemical transformations like rigid and practically did not blow up in the organic solvents. Elemental analysis (%) Found: C 67.64, H 5.17, N 7.26, S 3.73; Calcd. for C_9H_7NS, C 67.08, H 8.69, S 19.87.

The much pronounced decreasing of N and S percentages in the polymer is undoubtly linked to the phenomenon of degradation and oxidation of the product containing -NCS groups, which is confirmed by the definite diminishing of the characteristic stretching absorption band of isothiocyanate ν(NCS). In addition, more absorption bands are apeared at 1400-1100, 1730-1650 and 3400-3200 cm^{-1} relative to the oxidation process, attributed to (C-O), (C=O) and (O-H) groups, respectively.

The only difference with the polymers PITCS (1-3), the thermolysis of O-4-ITCS oligomers in the temperature range 158-240°C take place in exothermic manner with a weight loss of 13 %, but without a precise peak on the DTA curve (Fig. 1). The weight loss is interpreted by the degradation of carbamate groups contained in the oligomer composition.



$$-CH_2-\underset{C_6H_4-NHCOOC_2H_5}{CH}-CH_2-\underset{C_6H_4-NCS}{CH}- \xrightarrow{C_2H_5OH} -CH_2-\underset{C_6H_4-NCO}{CH}-CH_2-\underset{C_6H_4-NCS}{CH}-$$

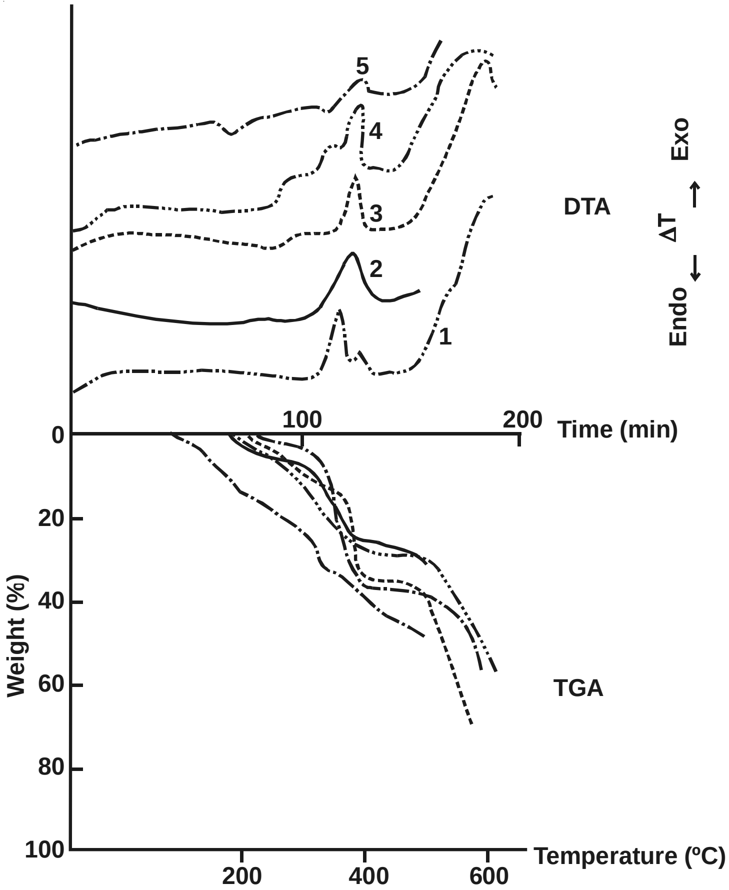


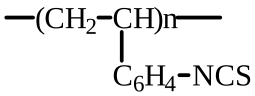
Fig. 1. DTA and TGA curves of polyisothiocyanato-styrene (PITCS)
1. P-2-ITCS 2. P-3-ITCS 3. P-4-ITCS 4. P-2,4-DITCS 5. O-4-ITCS

According to the thermogravimetric study of poly-N-(4-vinylphenylethyl)carbamate, most of the ethanol units released the suggested temperature range. The elemental analysis and the thermogravimetric study permit us to conclude that the synthesized O-4-ITCS oligomer enclose about 55.6% of -NCS isothiocyanate groups.

In the second stage, within the temperature range of 240-430°C, the partially cross-linked polymers undergo exothermically (Table-1). It is noted that in DTA curves, the PITCS (1 and 4) enclosing the isothiocyanate groups at the *ortho*-position caused one exothermic effect. Whereas the thermolysis of polystyrene occurs through an endothermic effect. The weight loss for the P-2-ITCS is about 35 %, slightly greater than that for the P-2,4-DITCS; the polystyrene undergoes in general a depolymerization[18], which is due to its high weight loss (94 %).

TABLE-1

RESULTS OF THERMAL GRAVIMETRIC ANALYSIS OF POLYISOTHIOCYANATO-STYRENE (1-5):



$$-(CH_2-\underset{\displaystyle C_6H_4-NCS}{\underset{|}{C}}H)_n-$$

No.	Polymer	[η] dL/g	Stage	Peak nature by DTA	$T_{beginning}$ (°C)	$T_{max.}$ (°C)	$T_{end.}$ (°C)	Loss mass (%)	Maximum exo peak total decomposition (°C)
1	P-2-ITCS	0.26	1	Exo	240	350	410	35.0	590
2	P-3-ITCS	0.24	1	Exo	240	285	350	11.0	590
			2	Exo	350	370	430	24.0	
3	P-4-ITCS	0.32	1	Exo	230	300	360	10.5	600
			2	Exo	360	385	420	21.0	
4	P-2,4-ITCS	0.28	1	Exo	200	300	430	28.0	595
5	O-4-ITCS	0.11	1		158	205	245	15.5	590
			2	*	287	315	360	13.0	
			3		360	385	410	8.0	
6	PS	0.28	1	Endo	265	350	400	94.0	370

*The process is accompanied with exothermic effect (not clear).

The general weight loss for the PITCS depends on the position of -NCS groups in the monomer unit, it decreases in the order:

P-2-ITCS (35.0 %) > P-4-ITCS (31.5 %) > O-4-ITCS (21.0 %)

the loss is weak for the oligomer, which offers a mobility of macromolecular segments and high aptitude for the reticulation of chains.

This observation is emphasized by the weight loss variation curves in function of temperature elevation of poly(vinylphenyl)isothiocyanato-styrene (Fig. 2).

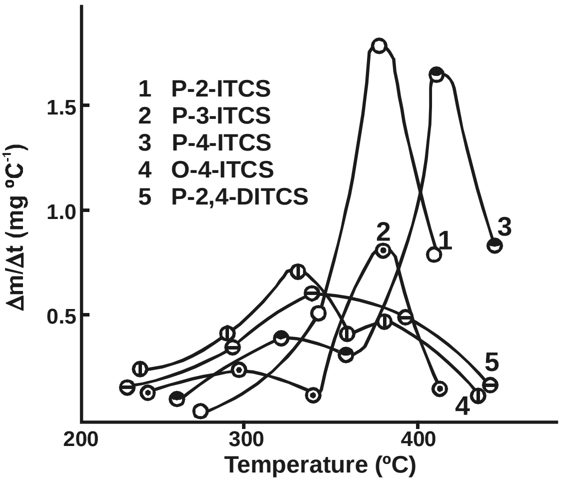


Fig. 2. Curves of the speed variation of the weight loss in function with the temperature of the polyisothiocanato-styrenes (PITCS)

It is noted that the curves 1 and 5 are similar, nevertheless with increasing of the temperature and the increase of the reticulation power for O-4-ITCS (2). The weight loss speed is apparently less than that of P-4-ITCS; for the curves of P-3-ITCS (2) and of P-4-ITCS (1) appears two maxima at low temperatures, T = 300 and 330°C, and at high temperatures, T=380 and 420°C, respectively. This displacement of temperature is linked undoubtly to the difference of reticulation rate, which is pronounced for the P-4-ITCS (the -NCS groups acquire weah steric cluttering, which facilitate the creation of reticulation bonds). The curves, $\Delta m/\Delta t = f(T)$, for the P-2-ITCS (3) and the P-2, 4-DITCS (5) slightly differently develop, that is with one maximum. While for the P-2-ITCS at the temperature T = 380°C, the weight loss speed is greater than the P-3-ITCS. Maximal loss speed for the P-2, 4-DITCS is reached at 350°C; it increases slowly and decreases slowly. It has also been observed that -NCS groups contribute to accenting and reinforcement of reticulation phenomenon.

The chromatographic analysis of destruction products of PITCS (1-3) showed that a collected pyrolytic products, in the range temperature 350-410°C, contains benzene, styrene, phenylisothiocyanate, 2-, 3- and 4-vinylphenylisothiocyanate and certain unidentified compounds. The quantity of monomers in the pyrolysat reaches 11-24 %.

Conclusions

The poly-2, poly-3, poly-4-vinylphenylisothiocyanato-styrene, by the increasing of temperature till 230°C, are transformed into three dimensional structure without a weight loss, then decrease slowly and that the temperature of their total destruction exceeds that of polystyrene by 220-230°C, the weight loss speed depends very tightly on the position of -NCS groups and decreases during the passage of the *ortho*- and *para*-isomer then at the oligomer of 4-isothiocyanato-styrene.

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