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Thermogravimetric Analysis of Poly-N-(4-vinylphenyl)alkyl Dithiocarbamates

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Poly-N (4-vinylphenyl)alkyl dithiocarbamates was prepared by radical polymerization. The chemical structures of the polymers were characterized by FT-IR spectroscopy and elemental analysis. The physical properties of polymers including solution viscosity, thermal stability and thermal behaviour were studied as well. The polymer showed an excellent stability. Their inherent viscosities were in the range of 0.7-1.0 dL/g. Thermal study of the poly-N-(4-vinylphenyl)-alkyl dithiocarbamates and their copolymers with styrene and isothiocyanatostyrene shows an elimination of alkyl mercaptans at the first stage but at the second stage we observe a reticulation of chains of the macromolecules during the thermolysis process. We observe also that the temperature of the total destruction of the poly-N-(4-vinylphenyl)alkyl dithiocarbamates and copolymers increases about 250 ºC comparatively to the polystyrene.

Key Words: Poly-N-(4-vinylphenyl)alkyl dithiocarbamates, Thermal gravimetric, Polystyrene, Thermal stability, Cross-linking.

INTRODUCTION

The polystyrene (PS) has a weak adhesion on the surfaces of metals, glasses and others[1]. On the intention of the plastification and the increase of adhesion in its composition, we introduce groups such as: -NHCXYR (X, Y = oxygen, sulphur; R = alkyl). These groups represent a stabilizing action and thermal stability[2,3]. However, many other non-sulphur cross-linking (*e.g.*, the bisperoxycarbamates) agents have been developed[3]. The bisperoxycarbamate as cross-linking agents in natural rubber has been used by Hepburn[4,5] and Amu and Hepburn[6]. The introduction of the functional group carbamate or thiocarbamate within the macromolecule of polymer

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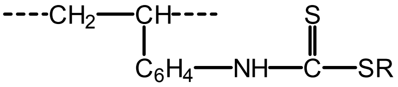
increases their thermal stability but the comparative stability at high temperature is not identified. It is also reported in the literature that the use of hexamethylene-N,N'-*bis*(*t*-butyl peroxycarbamate) as cross-linking agents for fluoroelastomer[7-9]. On the other hand the presence of these functional groups will make these polymers cross-linkable and the resulting polymers have not a good thermal stability, but it has the possibility to be converted to the thermally stable materials *via* cross-linking processes

In addition, on heating the alkyl dithiocarbamates groups may release the alkylmercaptans (thiols), but the thermal behaviour of the polymers carrying the functional groups -NHC(S)-SR, has not intensively studied. In this context, an interest is given to study of the poly-N-(4-vinylphenyl)-alkyl dithiocarbamates (**I-III**):



$$\text{----}CH_2-\underset{\displaystyle C_6H_4-NH-\overset{\displaystyle S}{\overset{\|}{C}}-SR}{\underset{|}{CH}}\text{----}$$

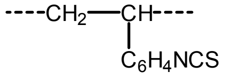
where, R = CH_3 (**I**), C_2H_5 (**II**), C_4H_9 (**III**)

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 in cyclohexanone as solvent at 30 ºC using an Ostwald viscosimeter. The infrared spectra were recorded on Shimadzu 435 IR spectrophotometer. The infrared (FT-IR) spectra of the samples dispersed in dry KBr pellets were recorded in 4000-400 cm^{-1} region. Differential thermal (DTA) and thermo-gravimetric analysis (TGA) measurement were performed with Shimadzu DTA-50 and TGA-50 thermal analyzers, respectively. The DTA measurement proceeded at a heating rate of 10 °C/min in air, whereas the TGA measurement proceeded at a heating rate of 10 °C/min under nitrogen. A Shimadzu GC-9A gas chromatographer 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 were used for the chromatographic analysis of pyrolysat obtained in the range of temperature 280-420 ºC.

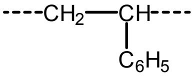
Polymer and copolymer synthesis: The mixture of 5×10^{-2} mol of monomer N-4-vinylphenyl alkyldithiocarbamate, 2 mL of cyclohexanone distilled before use and azobisisobutyronitrile (AIBN, [**I**] = 2 mol %) was used as an initiator. After the elimination of air from reaction area, the Pyrex glass ampoules 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 of appropriate *n*-hexane solvent. The precipitated polymer was collected and dried in vacuum at 50 °C for 1 h till the stabilization of its weight[10].

The yield of the polymers (**I-III**) reaches 95 %. By the same procedure we have obtained the copolymers of styrene (**VI, VII**) containing 30 mol % of -NHCSSCH$_3$ groupings, homo polymers of 4-isothiocyanato-styrene (**IV**) and styrene (**V**).



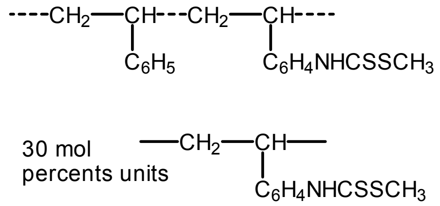
$-\!-\!-\!-CH_2-\underset{C_6H_4NCS}{\underset{|}{C}H}-\!-\!-\!-$

Copolymers **IV**



$-\!-\!-\!-CH_2-\underset{C_6H_5}{\underset{|}{C}H}-\!-\!-\!-$

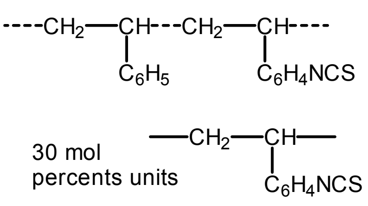
Copolymers **V**



$-\!-\!-\!-CH_2-\underset{C_6H_5}{\underset{|}{C}H}-\!-CH_2-\underset{C_6H_4NHCSSCH_3}{\underset{|}{C}H}-\!-\!-\!-$

30 mol percents units $-CH_2-\underset{C_6H_4NHCSSCH_3}{\underset{|}{C}H}-$

Copolymers **VI**



$-\!-\!-\!-CH_2-\underset{C_6H_5}{\underset{|}{C}H}-\!-CH_2-\underset{C_6H_4NCS}{\underset{|}{C}H}-\!-\!-\!-$

30 mol percents units $-CH_2-\underset{C_6H_4NCS}{\underset{|}{C}H}-$

Copolymers **VII**

The elimination's kinetics of the alkyl mercaptans (thiols) of polymers in the form of films with 40-50 μm thickness on the KBr pellet, has been studied by varying the intensity of stretching band (characteristic peak) at ν(NCS), 2250-2100 cm^{-1} in relation to ν aromatic C=C stretching band, 1605-1600 cm^{-1}, during the time.

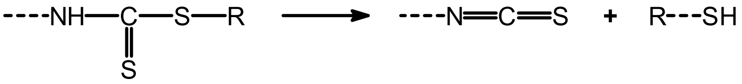
IR spectra of all poly-N-(4-vinylphenyl)alkyl dithiocarbamates and their copolymers contain prominent characteristic bands which indicate stretching vibrations of aliphatic C-H at 2967-2909 cm^{-1}, aromatic C-H at 3060 cm^{-1}, characteristic absorption peaks N-H at 3400-3350 cm^{-1} (strong), 1225 cm^{-1} N-H stretching, 1108 cm^{-1} C-N stretching, 1225-1190 cm^{-1} C=S stretching.

The elemental analysis results are also in good agreement with the structure of polymers and with calculated percentages for carbon, hydrogen, nitrogen, sulphur contents in polymer repeating unit of poly-N-(4-vinylphenyl)alkyl dithiocarbamates;

(**I**) (%): S 30.47 (30.62), C 57.39 (57.41), H 5.27 (5.26), N 6.68 (6.69).
(**II**) (%): S 28.62 (28.70), C 59.13 (59.19), H 5.79 (5.82), N 6.22 (6.28).
(**III**) (%): S 25.32 (25.49), C 62.07 (62.15), H 6.68 (6.77), N 5.52 (5.58).

RESULTS AND DISCUSSION

The data of the thermogravimetric analysis showed that in the temperature range of 110-230 °C, the polymers PVPTC (**I-III**), respectively release amounts of alkyl mercaptans (thiols) in agreement with the theoretical data (Table-1).



$$\text{----NH—}\underset{\underset{\displaystyle S}{\|}}{C}\text{—S—R} \longrightarrow \text{----N=C=S} + \text{R---SH}$$

TABLE-1
RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF POLYMERS PVPTC (**I-V**) AND COPOLYMERS (**VI, VII**)

No.	X	η (dL/g)	Stage	Peak nature by DTA	$T_{beginning}$ (°C)	T_{max} (°C)	T_{end} (°C)	Loss mass (%)
I	$NHCSSCH_3$	0.8	1	Endo	110	160	220	23.0 (22.9)*
			2	Exo	220	300	390	16.0
			3	Exo	390	420	450	4.0
			4	Exo	450	590	710	57.0
II	$NHCSSC_2H_5$	0.9	1	Endo	110	170	220	27.0 (27.8)
			2	Exo	220	290	370	14.0
			3	Exo	370	400	460	10.5
			4	Exo	460	605	750	48.5
III	$NHCSSC_4H_9$	0.7	1	Endo	110	180	230	35.0 (35.8)
			2	Exo	230	300	370	13.0
			3	Exo	370	410	450	8.0
			4	Exo	450	580	660	44.0
IV	NCS	2.6	1	Endo	260	305	365	13.5
			2	Exo	365	380	480	22.0
			3	Exo	480	625	880	64.5
V	H	2.2	1	Endo	260	370	410	93.0
VI	H: $NHCSSCH_3$ (70:30)	1.0	1	Endo	115	165	210	9.0 (7.0)
			2	Exo	210	395	450	49.0
			3	Exo	450	550	640	42.0
VII	H:NCS (70:30)	1.2	1	Endo	230	390	470	64.0
			2	Exo	470	580	695	35.0

*Theoretical loss weight volatile products alkyl mercaptans (thiols).

This is confirmed by the endothermic peak on the curve DTA and the weight loss appearing on the curve TGA. After then it appears, in the range of 230-750 °C, three exothermic peaks on the DTA curve. Exothermic variations are observed just after the elimination of alkyl mercaptans in all polymers between 230-750 °C. The first stage, in the interval 230-390 °C, is linked to the exothermic reticulation (of the polymer: poly-4-isothiocyanatostyrene)[11]. The second stage, in the range of 390-450 °C, is less intense than the first (5-10 %) and without any increasing in weight loss. The third stage exothermic peak, in the range 450-750 °C, is attributed to the thermo oxidative destruction of reticulated polymer, whereas the weight residue of the remaining polymer transforms to a volatile gas product.

The processes which intervene during the thermolysis of polymers (**I-III**) are illustrated by the speed's variation of the weight loss [$\Delta m/\Delta t = f(T)$] in function of temperature (Fig. 1). On the curves, $\Delta m/\Delta t = f(T)$, it appears four attributed to endothermic and exothermic effects. The first maxima, (endothermic effects), the clear ones reflect the rapid elimination of alkyl mercaptans.

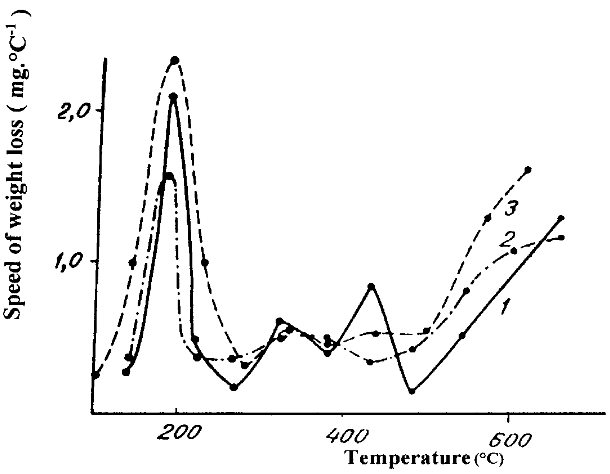


Fig. 1. Curves of the speed variation of the weight loss in function with the temperature of the poly-N-(4-vinylphenyl) alkyl dithiocarbamates
(**1**) Poly-N(4-vinylphenyl)methyl dithiocarbamate
(**2**) Poly-N(4-vinylphenyl)ethyl dithiocarbamate
(**3**) Poly-N(4-vinylphenyl)butyl dithiocarbamate

Going from radical methyl of polymer **I** to radical butyl in polymer **III**, the rupture speed of the organic product increases, this has been confirmed by kinetic data using the FT-IR spectroscopy (Fig. 2). This phenomenon explained by the decrease of intermolecular force interactions during the increase of radical size, or the increase of radical molecular weight.

Similarities of the curves [$\Delta m/\Delta t = f(T)$] of the polymers **I-III**, after the elimination of alkyl mercaptans and the poly-4-isothiocyanato-styrene curve, in the range 230-750 °C, permits us to conclude that the thermolysis concerns materials which differ less in composition and structure.

An analogous analysis for the copolymers of styrene **VI** containing 30 mol % of the N-(4-vinylphenyl) methyl dithiocarbamate unit has shown a similarity in the behaviour with the homo polymers (Table-1). By heating until 230 °C, the copolymer **VI** releases the methyl mercaptan CH_3SH in quantity nearly equals to theoretical one and the IR spectra show a broad intense peak in 2250-2000 cm^{-1} region which covers the area of the -NCS

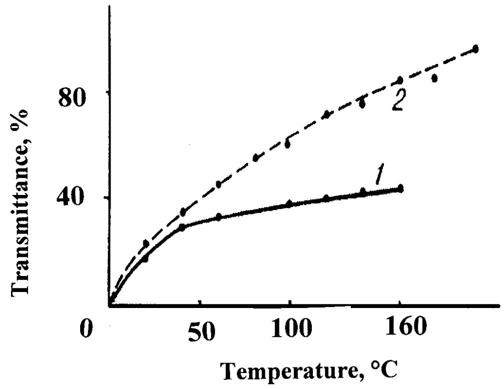
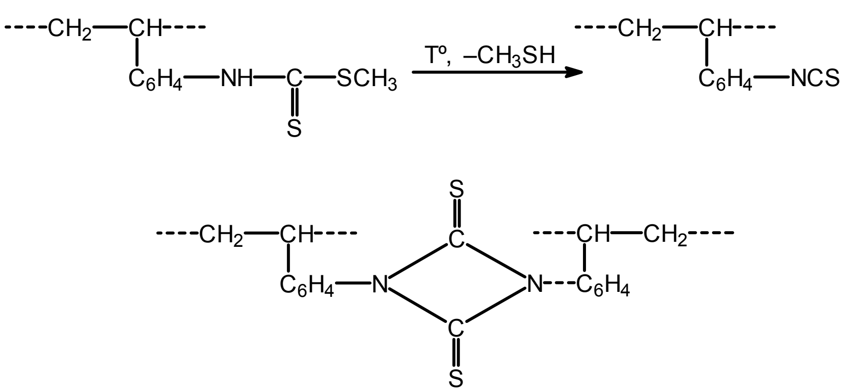
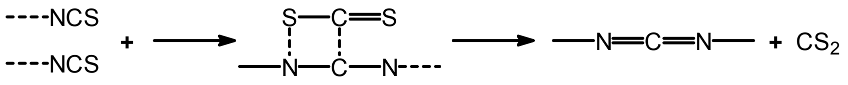


Fig. 2. Speed of getting groups -NCS in the poly-N-(4-vinylphenyl) alkyl dithiocarbamates at 112 °C
(**1**) Poly-N-(4-vinylphenyl)methyl dithiocarbamate
(**2**) Poly-N-(4-vinylphenyl)butyl dithiocarbamate

group and at the same time the broad peak due to N-H group in -NHC(S)SCH_3 at 3350 cm^{-1}, so the copolymer **VI** transforms practically to copolymer **VII** with the same composition of 4-isothiocyanato-styrene units. At the temperature range of 230-470 °C, the thermolysis of these copolymers is less different. This is probably due to macromolecular weight values which are close to each other. However, the copolymer differs from the homo polymers **IV** and **V**; this is clear comparing to the TGA curves (Fig. 3). The fact that the polymers **VI** and **VII**, by heating until 420-450 °C, lose in weight nearly two times less than the polystyrene **V**, but two times more than the poly-4-isothiocyanato-styrene **IV**. This is due to a deep reticulation of the macromolecule composed from 4-isothiocyanato-styrene units during the process of thermolysis. The phenomenon of reticulation involves two stages. The first, is realizing up to the temperature of 240 °C by obtaining of dimers (dimerization) of -NCS groups according to the following scheme:



The second, at a high temperature, followed by the dissociation of dimers and obtaining stable carbodiimide group[12-20].



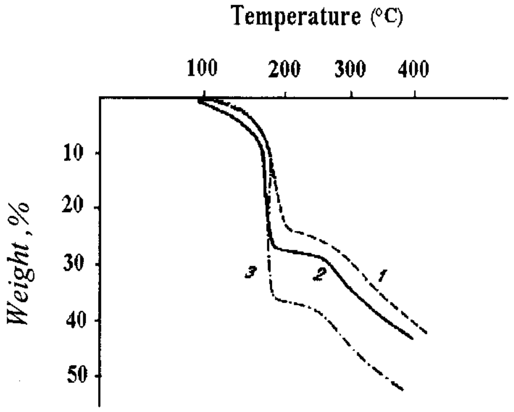


Fig. 3. Thermograms curves (TGA) of poly-N-(4-vinylphenyl)alkyl dithiocarbamates (PVPTC)

This fact is confirmed by chromatographic analysis of the thermolysis products at 250 °C where CS_2 has been detected.

The pyrolysis chromatographic analysis of copolymers **VI** and **VII**, obtained in the temperature range of the de-polymerization of polystyrene (230-420 °C), shows an analogy of pyrolysis products. These are the styrene, the ethyl benzene, the toluene and the dimers of styrene as in the case of the polystyrene[21].

The pyrolysat contains also a low quantity of 4-isothiocyanato-styrene monomer and of 4-ethyl phenyl isothiocyanate compound.

There is a reason to point out that for the homo-polymer **IV**, the quantity of 4-isothiocyanato-styrene monomer is low and can not exceeds[10] the 11%.

Conclusion

Some of the methods are available in literature[3,22-24] to improve the thermal stability of certain categories of polymers which are carried out with a chemical modification of their structure by introducing of active functional groups, *e.g.*, isocyanates, thioureas, carbamates, *etc*. In fact, typical polystyrenes are known to exhibit small resistance to heat. This low heat resistance is the main reason of relatively limited technical applicability of these polymers. In this work, we tried to improve thermal properties of polystyrene polymers. In conclusion, the thermal treatment of polystyrene containing alkyl dithiocarbamates groups, leads first to the elimination of alkyl mercaptans (until 230 °C) and a reticulation of macromolecules (230-450 °C) followed by a partial dimerization, of –NCS groups, then by the obtaining of carbodiimides groups with a low weight loss and finally a total decomposition occurs in the vicinity of 750 °C and the temperature of the total decomposition of poly-N-(4-vinylphenyl)alkyl dithiocarbamates exceeds that of the polystyrene by 250 °C.

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