

THERMAL AND KINETIC STUDY OF THE POLY VINYL PHENYL DITHIOCARBAMATS TRIETHYL-AMMONIUM

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ABSTRACT

The present paper was treats to the thermal study of the poly-vinylphenyl dithiocarbamats triethylammonium (PVPDT) and their respective monomers. The PVPDT was prepared is polyaminostyrene by chemicals reactions, synthetic procedures for the preparation were described. 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 excellent stability. Their inherent viscosities were in the range of 0,7 – 1.0 dL/g. Thermal study of the polymers show that at the first stage of the thermolysis process, there is an elimination of the triethylamine and the carbon disulfide. The kinetic parameters of the elimination process have been evaluated using the theoretical Horowitz-Metzger method. At the second stage, the obtained monomer undergoes a polymerization according to a Zwitter-ion mechanism.

Keywords: Analysis, vinyl phenyl dithiocarbamats, activation energy, thermo gravimetric.

INTRODUCTION

The compounds vinylphenyl dithiocarbamats of ammonium and triethylammonium find an application in the synthesis of monomers such the vinylphenylisothiocyanates^{1,2}. For an experimental systematization of a synthesis materiel, a great interest is given to the properties of these compounds and their composition. The polystyrene PS has a weak adhesion on the surfaces of metals, glasses and others³. On the intention of the plastification and the increase of adhesion in its composition, we introduce groups such as: -NHXYR (X, Y = oxygen, sulphur; R = alkyl). These groups represent a stabilizing action and thermal stability^{4,5}. However, many other non – sulphur cross-linking (for example the bisperoxycarbamates) agents have been developed⁵. The bisperoxycarbamate as cross-linking agents in natural rubber has been used by Hepburn C.^{6,7} and Amu A. et al⁸. The introduction of the functional group carbamate or thiocarbamate within the macromolecule of polymer increases their thermal stability but the comportment at high temperature is not identified. Also it is reported in the literature that the use of hexamethylene-N, N' bis (tert-butyl peroxycarbamate) as cross-linking agents for fluoroelastomer⁹ and Yeganeh H. et al.¹⁰, Mallakpour S.F. et al¹¹), 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. However, PS are generally known that they offer little resistance to heat, which causes the disappearance of their properties from about 100 to 120°C and which limits relatively their technical applicability. Thus thermal stability of PS has received extensive attention. One accepted approach for the improvement of thermal stability of PS is the chemical modification of their structure by introducing functional groups into the aromatic cycle. Many works have been carried out and showed the effect of the functional groups on the

thermal stability of polymers^{12,13}, for example Tamami et al.¹⁴ were 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. In this work we give the results thermo gravimetric analysis of the vinylphenyldithiocarbamats (VPDT)², the polyvinylphenyl dithiocarbamats triethylammonium (PVPDT), and the kinetic parameters of the elimination process of organics compounds.

EXPERIMENTAL

Solvents and reagents

All chemicals were purchased from Aldrich and used after purification.

Apparatus

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 cyclohexanon as solvent at 30°C using an Ostwald viscosimeter.

IR spectra were recorded on Shimadzu 435 IR spectrophotometer. Spectre of solid was carried out using KBr pellets. The infrared (FT-IR) spectra of the samples dispersed in dry KBr pellets were recorded between 4000-400 cm^{-1} .

Differential thermal (DTA) and thermogravimetric analysis (TGA) measurement were performed in the temperature range, 20-800 °C, with Shimadzu DTA-50 and TGA-50 thermal analyzers, respectively. The DTA measurement proceeded at a heating rate of 5°C/min in air, whereas the TGA measurement proceeded at a heating rate of 5°C/min under nitrogen.

Was used a Schimadzu GC-9A gas chromatographer equipped with a flame ionization detector (FID).

The IR spectra of synthesized all PVPDT 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 3350-3400 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 PVPDT;

4-III (P-4-AS): C- 80.65% (80.67%), H- 7.53 % (7.56%) , N- 11.50 % (11.76%)

3-II (P-3-VPDT): S- 21.32% (21.62%), C- 60.21% (60.81%), H- 8.01% (8.11%), N- 9.23% (9.46%)

4-II (P-4-VPDT): S- 21.42% (21.62%), C- 60.53% (60.81%), H- 8.07% (8.11%), N- 9.33% (9.46%).

(): calculated value

Polyaminostyrol synthesis

The mixture of $5 \cdot 10^{-2}$ mol of monomer 4 - aminostyrene (4-AS), 2ml of cyclohexanon distilled beforehand and azobisisobutyronitrile (AIBN, [I] = 2 mol percent) 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 (6h), 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 during one hour till the stabilization of its weight¹⁵.

By the same procedure we have obtained the polymers: poly ortho aminostyrol (P-2-AS) and poly meta aminostyrene (P-3-AS)¹⁶. The yield of the polymers (III) reaches 95%.

Polyvinylphenyl dithiocarbamats (PVPDT) synthesis

The samples of polymers were obtained at a room temperature for five hours by the addition of 1.19 g of polyaminostyrene, 4 ml of dimethylformamide DMF, 2.5 ml of triethylamine and 0.7g of carbon disulfide CS_2 . The polymer obtained is precipitated in ether solution, after filtration we keep it in ether containing 5% of triethylamine for one hour at the temperature from 5 to 10°C. We recommence this procedure two times, after the polymer is dried under vacuum at the precedent temperature until stabilization of the weight¹⁶.

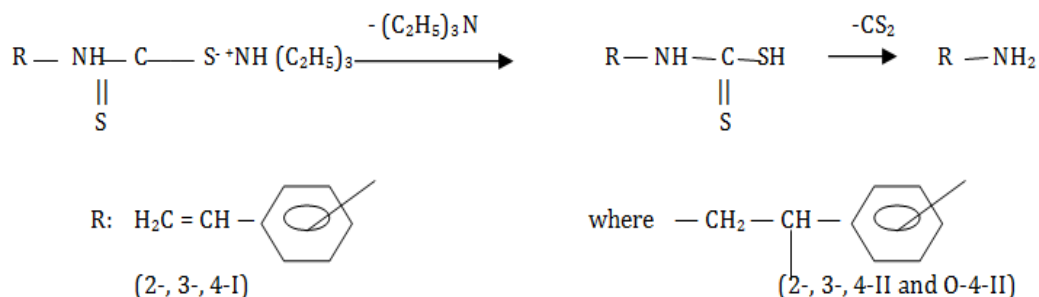
Oligomer synthesis

Oligomer O-4-II prepared, is oligomer 4-aminostyrene (O-4-III) (degree of polydispersity $n=30$) by the action of carbon disulfide and the triethylamine an analogue with the precedent method.

Elemental analysis: Calculated for O-4-II, S- 14, 3%, for O-4-III, N- 8, 97%.

RESULTS AND DISCUSSION

The results showed (Table1) that the destruction process of the compounds monomers vinylphenyl dithiocarbamats triethylammonium (VPDT) (I) passed through two stages. First, in the range of the temperature from 50 to 85°C, for all the compounds, there is an endothermic effect on the curves DTA which shows (weight loss) on the curve TGA, a rupture of the triethylamine and the carbon disulfide compounds. This stage of the thermolysis process is illustrated as follow way:



In the Table 2, have been defined for each eliminate compound the kinetic parameters: energy activation E_a , order reaction n , speed constant K , pre exponential factor Z , and temperature T . First the parameters were defined for the triethylamine $(\text{C}_2\text{H}_5)_3\text{N}$, second for carbon disulfide CS_2 .

The identification and the detection of evolved gaseous products has been realized by chromatography by analysis products degradation polymers PVPDT, and the elimination of gaseous is deduced from TGA curves of the polymers, the endothermic effect on the curves DTA leading to the elimination of CS_2 and $(\text{C}_2\text{H}_5)_3\text{N}$ with weight loss. The values of this weight loss are near to calculated theoretical values.

Table 1: Results of the thermal gravimetric analysis of VPDT (I), PVPDT (II) Triethylammonium and polyaminostyrenes PAS(III)

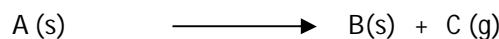
Compounds	Interval of temperature °C	Weight loss, %	Tenor of the transformation, %	Mass of the residue (%) at 200°C	Temperature of the total decomposition, °C
2-I	60-80	57	96	1	170*
3-I	70-95	56	95	4	195*
4-I	75-95	55	95	45	520
2-II	90-200	27	47	73	550
3-II	95-200	42	75	58	550
4-II	100-170	51	86	49	530
0-4-II**	80-200	37	62	63	
	110-190	2	-	98	530
2-III	230-255	-	-	98	
	265-430	31	-	67	650
	135-190	2.5	-	97.5	
3-III	260-330	-	-	97.5	660
	330-430	24	-	75.5	
	110-195	3.5	-	96.5	
4-III	240-300	-	-	96.5	680
	300-430	14	-	82.5	
0-4-III**	120-155	2.5	-	97.5	
	260-410	52	-	45.5	600

*Evaporation temperature of the residue **Oligomer

The weight loss permitted to us to find a purity degree from 95 to 96% for the compounds (I) (Table 1). Then we can conclude that the vinylphenyldithiocarbamats (I), kept at open air, are partially decomposed following the above scheme. The kinetic parameters of the elimination reaction of the triethylamine and the carbon disulfide for the vinylphenyl dithiocarbamats VPDT have been calculated using the Horowitz-Metzger method¹⁷ (Table 2). The energy activation E_a and the constant K increase from 2-I to 4-I compounds. We remark that for the compound 4-I, the values of energy activation E_a , pre exponential factor Z and speed constant K exceed their similar 3-I and 2-I.

The kinetic parameters of the first process of elimination are described by the Horowitz-Metzger method as following:

For a chemical reaction:



The reaction speed is:

$$\frac{dC}{dt} = -KC^n \quad -1-$$

$$K = Z \cdot e^{-E_a/RT} \quad -2-$$

Where:

C: is the proportion or the fraction of the compound A(s) decomposed in the time t.

K: speed constant of the reaction.

n: reaction order.

R: universal constant of gaseous 8.31 J/K.mol.

T: absolute temperature, K.

Z: pre exponential factor.

E_a: activation energy, kJ/mol.

At the thermogravimetric search, the dependence between the time and the temperature of the solid substance is definite by the linear speed

$$q = \frac{dT}{dt} \quad (\text{grad/min.})$$

Then we deduce from -1-

$$\frac{dC}{dt} = -\frac{Z}{q} e^{-\frac{E_a}{RT}} dT \quad -3-$$

By integration of the equation -3-

$$\int \frac{dC}{dt} = -\int_0^T \frac{Z}{q} e^{-\frac{E_a}{RT}} dT \quad -4-$$

The integration of the right hand side of the equation -4- is impossible. To render this possible we make an approximation calculation. Horowitz and Metzger propose to change the expression 1/T by:

$$\frac{1}{T_s + Q} = \frac{(1 - \frac{Q}{T_s})}{T_s} \quad \text{with} \quad \frac{Q}{T_s} \ll 1 \quad -5-$$

Where

T_s: is the fixed temperature of each case.

Q: is the variation on both sides of the temperature T_s.

The right hand of the equation -4- becomes:

$$\int \frac{Z}{q} \exp\left[-\frac{E_a(1 - \frac{Q}{T_s})}{RT_s}\right] dQ = \frac{Z}{q} \exp\left(-\frac{E_a}{RT_s}\right) \cdot \frac{RT_s^2}{E_a} \cdot \exp\left(\frac{E_a \cdot Q}{RT_s^2}\right)$$

The integration of the first member of the equation -4- in the interval 0-T gives:

$$\frac{C^{1-n}}{1-n} = \frac{Z \cdot RT_s^2}{q \cdot E_a} \cdot \exp\left[-\frac{E_a}{RT_s} \left(1 - q \cdot \frac{Q}{T_s}\right)\right] \quad -6-$$

T_s: Temperature at which $\frac{dC}{dT}$ is maximal, then $\frac{d^2C}{dT^2} = 0$. This point is the maximum of DTG curve.

The concentration C at T = T_s is noted C = C_s.

$$\frac{Ea}{RT_s^2} = \left(\frac{Z}{q}\right) \cdot n \cdot C_s^{n-1} \cdot \exp\left(-\frac{Ea}{RT_s}\right) \quad -7-$$

$$\frac{C^{1-n}}{1-n} = -\frac{1}{n} \cdot C_s^{1-n} \cdot \exp\left(\frac{Ea \cdot Q}{RT_s^2}\right) \quad -8-$$

E_a and n values known we obtain from equation - 7 -, the pre exponential factor Z.

$$Z = \left[\frac{Ea \cdot q \cdot \exp\left(\frac{Ea}{RT_s}\right)}{RT_s^2 \cdot n \cdot C_s^{n-1}} \right]$$

This is due to the increase of the stability because of the increase of the acid properties of the 4-vinylphenyl dithiocarbamats relatively to the 2-I and 3-I isomers. We observe a decrease of activation energy E_a and pre exponential factor Z from 3-I to 2-I, due to the absence of conjugaison at the level structure. Because the vinylphenyl dithiocarbamats acids are intermediary instable compounds, we remark a slowly diminution of the kinetic parameters relatively to compounds (I) (Table 2).

Table 2: The kinetic parameters of the elimination reaction of the triethylamine and sulfide of carbon from the vinylphenyl dithiocarbamats triethylammonium compounds (VPDT)

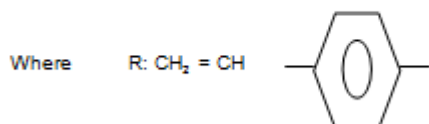
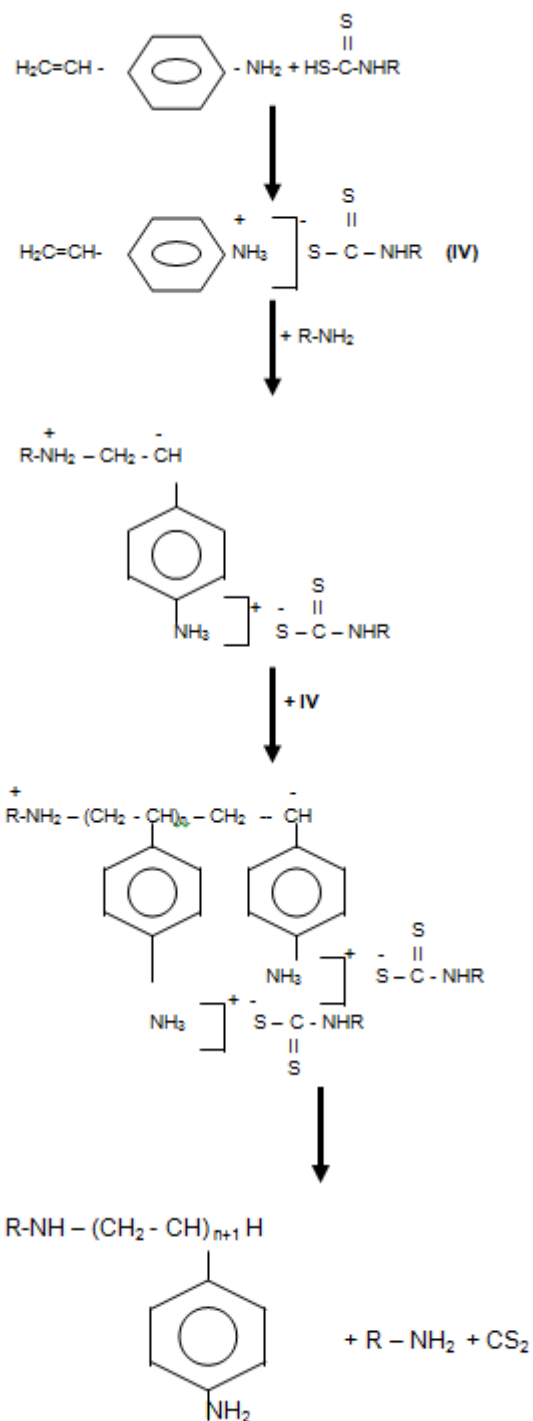
Compounds	Elimination reaction	T, K		Order n		E _a , kJ/mole		Z		K, s ⁻¹	
2-I	(C ₂ H ₅) ₃ NCS ₂	333	353	0.41	0.59	56	41	9 10 ⁵	2 10 ⁴	2.4 10 ⁻³	4.8 10 ⁻³
3-I	(C ₂ H ₅) ₃ NCS ₂	343	358	0.56	0.61	69	48	3 10 ⁷	1 10 ⁵	2.5 10 ⁻³	6.1 10 ⁻³
4-I	(C ₂ H ₅) ₃ NCS ₂	355	360	0.59	0.80	84	54	6 10 ⁸	4 10 ⁵	2.3 10 ⁻³	5.6 10 ⁻³

For the following stage of the thermolysis, we observe an evaporation of the aminostyrenes 2-AS (2-I) and 3-AS (3-I), we note that these aminostyrenes stem from the first stage of the decomposition. We remark an increase in the temperatures from 2-I to 4-I of the first and the second stages of the thermolysis process; this is probably due to the diminution of the volatility in the order 2-I, 3-I, 4-I from 2-AS to 4-AS. We shall expect to obtain the polyaminostyrenes 2-I, 3-I and 4-I. It is known, according to the literature data¹⁸, that the activity of the aminostyrenes (AS), for the radical reaction polymerization, increasing in the order 3-AS, 2-AS, 4-AS. Because the evaporation speed exceeds considerably the speed of the thermal polymerization of 2-AS and 3-AS, they give from 1 to 4% of polymer. We note that the mechanism of the last stage of the thermolysis process for the compound 4-I is not similar to the compounds 2-I and 3-I, we observe an increase until 520°C in the temperature of the total destruction of the residue. This phenomenon is due to the polymerization of the intermediary product of the thermolysis 4- aminostyrene (4-AS).

But in the thermolysis conditions, the polymerization speed of 4-AS is few upper than for 2-AS and 3-AS. The isomer para is twice or four more than the isomer ortho and meta.

This is an other mechanism polymerization of the monomer 4-AS. We can suppose that in the course of the thermolysis at interval temperature 60°- 70°C, the monomer 4-aminostyrene (4-AS) so obtained is polymerized by a cationic way. This mechanism is lonely identified for 4-AS during the polymerization in feebly acid middle¹

At the thermolysis process we obtain, from the 4-AS and the 4-vinylphenyl dithiocarbamat, the salt which is polymerized according a "Zwitter-ion" mechanism [1]:



We note that for a pure monomer 4-AS, this mechanism is in concordance with the experience. Like the monomers 2-AS and 3-AS, this monomer is practically not polymerized under the thermals conditions. The results of the thermolysis reactions of the polyvinylphenyl dithiocarbamats triethylammonium (II) confirm the suggested mechanism (Table1). Similarly to the case of the compounds VPDT (I), the thermolysis process of the compounds PVPDT (II) follow various stages: First, in the range of the

temperature from 90 to 200°C, there is an elimination of the triethylamine and carbon disulfide. The study of this stage permitted to determine, the probability of the reaction for obtain the PVPDT, if we calculate the weight loss. This is easy for the case of the 4-II but difficult for the 2-II, this is probably due to the steric encumbrement when we add the carbon disulfide and the triethylamine to the poly-2-aminostyrene with a good performance of 47%. To identify the second's stage process of thermolysis of the compounds (II), we treat the thermal gravimetric analysis of the polyaminostyrenes (III) (Table 2). We remark that the thermolysis follows similar stages to the compounds (III).

In the Table1, we give the thermal gravimetric data of the oligomers O-4-II and O-4-III; these oligomers have a little macromolecular mass relatively to their similar 4-II and 4-III. The thermolysis of these compounds follows similar stages, but we must remark that the temperatures of all the thermal effects are 20°C less than their similar 4-II and 4-III. This means that the temperatures ranges of the thermal transformations depend on the macromolecular weight of the polymers.

CONCLUSIONS

Some of the reported methods^{5,19-21} improve the thermal stability of certain categories of polymers were carried out with a chemical modification of their structure by introducing of active functional groups, for example, isocyanates, thioureas, carbamates, etc. In reality, 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 did contribute to improve thermal properties of polystyrene polymers, and finally a total decomposition occurs in the vicinity of 660°C and the temperature of the total decomposition of PVPDT exceeds that of the polystyrene by 240°C.

We remark again the formation of the 4-vinylphenyl dithiocarbamats triethylammonium (4-VPDT) during the thermolysis process and polymerization monomer no cationic way, according a zwitter-ion mechanism.

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