

Thermal Degradation of some Model Compounds for Polyvinylchloride

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SUMMARY

The thermal stability of some model compounds for polyvinylchloride with different types of structural defects was studied. The determinations were carried out in thermal dynamical conditions, using the conductometric detection of the evolved hydrogen chloride and thermogravimetric methods. The kinetic parameters corresponding to the first stages of dehydrochlorination reaction were discussed comparatively. The following thermal stability order was obtained: macromodels with $H_T >$ macromodels with $Cl_T >$ macromodels with Cl_A .

INTRODUCTION

The thermal stability of polyvinylchloride is highly influenced by its molecular structure. The monomer units normally polymerized, head to tail, are considered stable at higher temperatures than the temperature of beginning of the nonoxidative polymer degradation (AYREY et al. 1974).

The sites of the dehydrochlorination initiation may be different types of structural irregularities on the chain: branching, head to head structures, unsaturated groups, initiator fragments, ketoallylic chlorine groups, etc. (SVETLY et al. 1979, 1980, 1981).

The study of the low-molecular weight model compounds shows a much smaller activation energy of the dehydrochlorination for the branching structure products with tertiary chlorine as well as for the allylic chlorine products than for the secondary chlorine products (CHYTRY et al. 1969, 1970, 1971, 1973, THOMAS 1967, ROBINSON et al. 1978, ASAHINA and ONOZUKA 1964, 1964a, MAYER et al. 1971, SUZUKI et al. 1972).

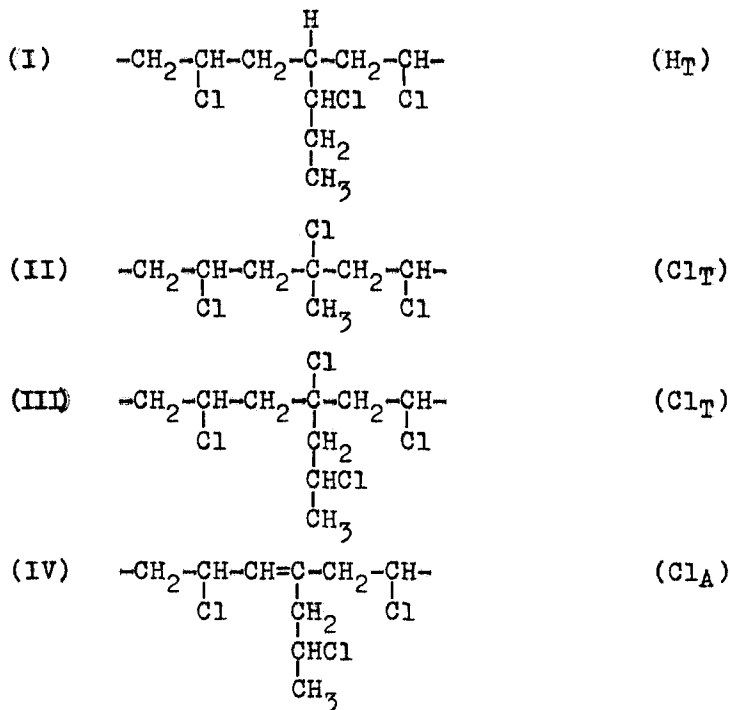
The studies conducted on the low-molecular weight model compounds give some informations regarding to the relative thermal stability of the different types of C-Cl bonds, but the extension on the polymer systems should be made carefully. For this reason, it is necessary to study the thermal stability of some macromolecular compounds having the type and the concentration of the structural defects well-known, in order to realize a reasonable correlation between the PVC structure and its thermal stability.

In this work we deal with the thermal stability of some macromodels for PVC - vinyl chloride copolymers - with struc-

tural defects deliberately introduced in macromolecule and in known amount.

EXPERIMENTAL

The following copolymers of vinyl chloride with 3-chloro-1-pentene (CARACULACU et al. 1978, BEZDADEA et al. 1974) (I), with isopropenyl chloride (CARACULACU 1966) (II), with 2,4-dichloro-1-pentene (CARACULACU et al. 1970) (III) and with 4-chloro-1-pentene (BURULIANA et al. 1977) (IV) were used as macromodels for polyvinylchloride:



The degradation of the samples and the detection of the evolved hydrogen chloride were performed with an apparatus described by BRAUN and THALLMAIER (1966). The thermal degradation was made in an inert atmosphere (argon) using a 0.2 g sample. The heating rate was 4.5°/min and it was obtained by means of a linear temperature programmer. The conductivity variation in time was followed by a recorder using the output of a Radiometer conductometer of CDM type.

The thermograms were recorded with a MOM Derivatograph, Paulik-Paulik-Erdey type, with the heating rate of 12°/min, in air. The sample weight was 50 mg.

The labile chlorine content was determined by phenolysis, according to a previous method (ROBILA et al. 1977).

RESULTS AND DISCUSSION

The dehydrochlorination rate in isothermal conditions will depend on the number of labile structures, which initiate the dehydrochlorination process. These structures can decompose at much lower temperatures than the temperature at which the determination is performed.

After the degradation is initiated, the propagation rate of dehydrochlorination on the chain will depend on the reaction temperature and not on the labile structure responsible for the process. Consequently, in order to compare the stability of various samples, the determinations must be made in isothermal conditions and at the same temperature. The measuring temperature must be high enough to allow the dehydrochlorination for the most stable samples. In such conditions, the samples of lower stability will begin to decompose before the moment when temperature becomes constant and the isothermal conditions are not realized.

On the other hand, it is expected that the decomposition of many primary defects takes place simultaneously at temperatures lower than the chosen temperature and therefore any distinction between their thermal behaviour will be concealed.

In order to avoid this undesirable defect, the decomposition at a constant rate heating proved to be a suitable method for PVC thermal stability (CARACULACU et al. 1978a). This method permits a correlation between the starting degradation temperature and the nature of defects responsible for dehydrochlorination.

The determination of evolved hydrogen chloride during polymer heating at a constant rate was made by a conductometric method (EGD method).

The starting dehydrochlorination temperature, ($T_{i,EGD}$), estimated as the temperature corresponding to the point of deviation from the base line of conductivity curve, can be used as a measure of thermal stability.

The results are shown on the Figures 1-3 and Table I.

The starting process of degradation occurs at different temperatures, depending on the polymer structure (Table I). Also the samples that decompose at higher temperatures have greater dehydrochlorination propagation rate than those which decompose at lower temperatures.

To compare the thermal stabilities of different samples we used the starting decomposition temperature estimated by two methods (EGD method, $T_{i,EGD}$, and thermogravimetric data $T_{i,TG}$, respectively) as well as the activation energy of the dehydrochlorination.

The activation energies were calculated by the Coats-Redfern (ECR) (COATS and REDFERN 1964) and REICH-LEVI (ERL) (REICH and LEVI 1963) methods. The first method was used to estimate the total activation energies from thermogravimetric data and the second was used to characterize the first stages of the dehydrochlorination reaction.

In these calculations, in the EGD method, the hydrogen chloride amount evolved in the domain of very small decomposition degrees of samples ($\alpha = 0.6 \cdot 10^{-4}$) was used. From the

TABLE I
Thermal stability of PVC macromodels

Sample	Cl _L (%)	T _{i,EGD} (°C)	T _{i,TG} (°C)	E _{CR} (kJ/mol)	n	E _{O,RL} ^{EGD} (kJ/mol)	E _{O,RL} ^{TG} (kJ/mol)
H _T copolymer	-	166	187	126.9	1.3	407.4	204.8
Cl _T copolymer	2.0	135	170	82.2	0.9	285.6	101.6
Cl _A copolymer initiator PB	-	109	125	48.5	0.0	193.2	79.4
Cl copolymer initiator TNBB	0.2	90					

thermogravimetical data, the transformation degree ($\alpha = w_t/w_\infty$ where w_t and w_∞ are the weight losses at a given moment of the reaction and at the end of the first decomposition stage, respectively) varied between 0 and 0.6.

The variation of E_{RL} values against the transformation degree for the PVC macromodels by the two methods is given in Fig. 1 and 2.

From the variation of T_i values, of the apparent activation energies (E_{CR}) and of the energies extrapolated to $\alpha = 0$ (E_{O,RL}) one can show that the thermal stability order is: H_T copolymer > Cl_T copolymer > Cl_A copolymer.

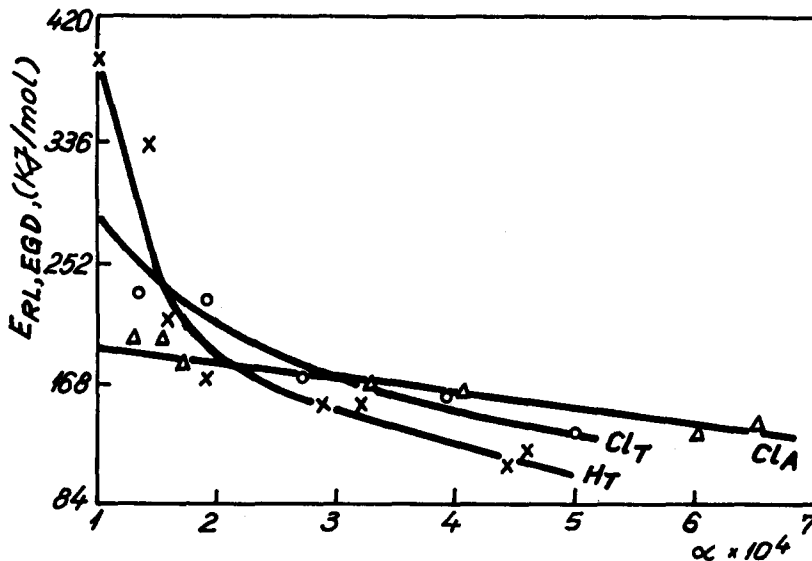


Fig. 1: E_{RL,EGD} versus α for PVC macromodels.

The apparent disagreement between the results obtained by the two methods is caused by the too limited range of values used for EGD determinations and for this reason the accuracy of area determination to calculate the activation energy is decreased.

The shape of the plots and the extrapolated values permit a good characterization of the macromodels.

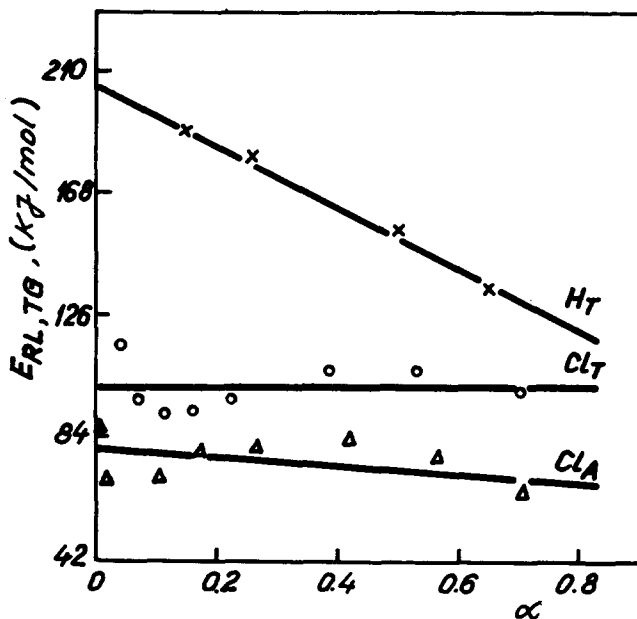


Fig. 2: $E_{RL, TG}$ versus α for PVC macromodels.

Also, one can notice that the activation energies corresponding to the first dehydrochlorination stages have greater values than the total energies.

The maintenance of the same stability order for the whole temperature domain shows a very strong influence of the structural defect type on the thermal behaviour. This influence is very good evidenced by the DTG curves, which exhibit a rather marked inflexion for the H_T and Cl_T copolymers. The Cl_A copolymers show this inflexion at much smaller temperatures. The appearance of this inflexion is assigned to the presence of weak bonds in the polymer structure leading to the modification of the initiation stage (CARACULACU et al. 1970, SCHNEIDER 1978). This conclusion is evidenced from the aspect of E_{RL} plots against the transformation degree, which differ depending on the nature of the structural defect.

In the case of high concentration of structural defects, the duration of initiation process must be change and finally the dehydrochlorination reaction takes place at lower tempe-

ratures as results from the comparison of DTG curves (Fig.3) with those of a 10% Cl_T copolymer (CARACULACU et al. 1970).

The copolymers with tertiary hydrogen are the most stable at thermal degradation. We can concluded that the branching in PVC containing in the most part hydrogen at the tertiary carbon atom (ABBAS et al. 1975) should not influence the thermal stability of the polymer.

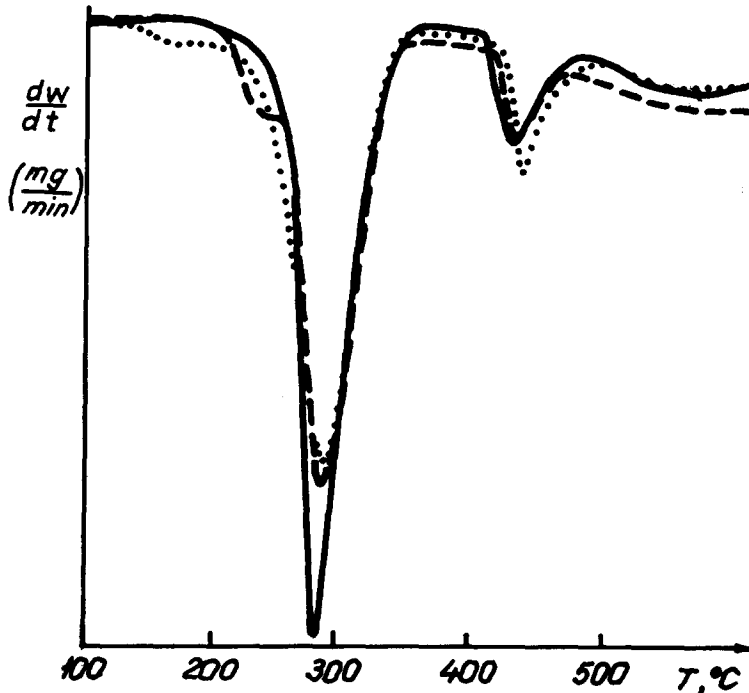


Fig. 3: DTG curves for PVC macromodels; — macromodel with H_T, --- macromodel with Cl_T, ... macromodel with Cl_A

Because the tertiary chlorine structures are in a very low concentration (below 0.2% monomer units) in PVC (BURUIANA et al. 1980), we can say that the thermal stability of the polymer will depend in a great measure on the allylic chlorine content.

Our results are in agreement with those of ASAHINA and ONOZUKA (1964) estimating the activation energies for the splitting of HCl for PVC micromodels. They found the same stability order: Cl_S > Cl_T > Cl_A.

REFERENCES

- ABBAS, K.B., BOVEY, F.A. and SCHILLING, F.C.: Makromol. Chem. Suppl. 1, 227 (1975)
- ASAHINA, M. and ONOZUKA, M.: J. Polym. Sci. A 2, 3505 (1964)
- ASAHINA, M. and ONOZUKA, M.: J. Polym. Sci. A 2, 3515 (1964a)
- AYREY, G., HEAD, B.C. and POLER, R.C.: J. Polym. Sci., Macromol. Rev. 8, 1 (1974)
- BEZDADEA, E., BRAUN, D., BURUIANA, E., CARACULACU, A. and ISTRATE - ROBILA, G.: Angew. Makromol. Chem. 37, 35 (1974)
- BURUIANA, E.C., AIRINEI, A., ROBILA, G. and CARACULACU, A.: Polym. Bull. 3, 267 (1980)
- CARACULACU, A.A.: J. Polym. Sci. A-1 4, 1829 (1966)
- CARACULACU, A.A., BEZDADEA, E.C. and ISTRATE, G.: J. Polym. Sci. A-1 8, 1239 (1970)
- CARACULACU, A., BURUIANA, E. and DOBRE, F.: Bul. Inst. Polit. Iași, s.II 24, 113 (1978)
- CARACULACU, A., BURUIANA, E.C., ROBILA, G., AIRINEI, A. and BARBINTA, V.: IUPAC Working Party on PVC Structure, Report to Cardiff Meeting, Sept. 19-22 (1978a)
- COATS, A.W. and REDFERN, J.T.: Nature 201, 68 (1964)
- CHYTRY, V., OBEREIGNER, B. and LIM, D.: Eur. Polym. J. Suppl. 379 (1969)
- CHYTRY, V., OBEREIGNER, B. and LIM, D.: Chem. Ind. 470 (1970)
- CHYTRY, V., OBEREIGNER, B. and LIM, D.: Eur. Polym. J. 7, 1111 (1971)
- CHYTRY, V., OBEREIGNER, B. and KRIVINKOVA, D.: Eur. Polym. J. 9, 649 (1973)
- MAYER, Z., OBEREIGNER, B. and LIM, D.: J. Polym. Sci. C 33, 289 (1971)
- REICH, L. and LEVI, D.W.: Makromol. Chem.: 66, 102 (1963)
- ROBILA, G., BURUIANA, E.C. and CARACULACU, A.A.: Eur. Polym. J. 13, 21 (1977)
- ROBINSON, P.J., SKELHORNE, G.G. and WALLER, M.J.: J. Chem. Soc., Perkin Trans. 349 (1978)
- SCHNEIDER, I.A.: J. Polym. Sci., Polym. Symp. 64, 95 (1978)
- SVETLY, J., LUKAS, R. and KOLINSKY, M.: Makromol. Chem. 180, 1363 (1979)
- SVETLY, J., LUKAS, R., MICHALCOVA, J. and KOLINSKY, M.: Makromol. Chem., Rapid Commun. 1, 247 (1980)
- SVETLY, J., LUKAS, R., POKORNY, S. and KOLINSKY, M.: Makromol. Chem., Rapid Commun. 2, 149 (1981)
- SUZUKI, M., TSUGE, S. and TAKEUCHI, T.: J. Polym. Sci. A-1 10, 1051 (1972)
- THOMAS, P.J.: J. Chem. Soc. B 1238 (1967)

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