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THE THERMOGRAVIMETRIC BEHAVIOUR OF THE VINYL ACETATE AND α-METHYLSTYRENE COPOLYMERS OF ACRYLONITRILE

C. Vasile, E. Maftei,* D. Gîlea and I. A. Schneider

Institute of Macromolecular Chemistry "P. Poni", Iassy, Roumania

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The influence of the copolymer nature, its comonomer content and the supermolecular structure on the thermal behaviour of the binary vinyl acetate and α-methylstyrene copolymers of acrylonitrile have been studied. The results have been correlated to granulometric and microscopic studies.

In the polyacrylonitrile fibre industry, copolymers of acrylonitrile are exclusively utilized instead of polyacrylonitrile homopolymer (PAN), because of great difficulties in colouring and the pronounced tendency to become yellow at relatively low temperatures. Nevertheless, the thermal behaviour of these copolymers has been little studied [1], although there are some comprehensive works on the mechanism of color changes to yellow [2] and of the thermal degradation of PAN [3].

This paper discusses first results concerning the thermal characterization of binary copolymers of acrylonitrile with vinyl acetate and α-methylstyrene using thermogravimetry.

Experimental

Binary copolymers of acrylonitrile with vinyl acetate (AN/VAc) and α-methylstyrene (AN/MS) have been prepared, the highest content of comonomer being 20% in the former and 40% in the latter case. The suspension polymerization was carried out in water for about 90 min, using a redox initiation system of persulphate-metabisulphite. The comonomer content was estimated spectrophotometrically and by the Kjeldahl method.

The relative viscosities were measured using 0.3% solutions in dimethylformamide at 25°, and for the thermogravimetric study those copolymers were chosen the viscosities of which were between 1.6 and 1.7 dl/g.

The thermogravimetric behaviour in air, using constant working conditions, was analyzed on a "MOM-Budapest" Derivatograph. The powdered polymer samples of known granulation were mixed with Al_2O_3 (just before calcination at over 1200°), which at the same time was also used as reference. The heating rate was maintained constant in all experiments, at 12.4°/min, in all cases the sample weight being 30 mg.

To use the corresponding DTA curves for the estimation of the heat of reaction, $NaNO_3$ was used for calibration. The latter shows two DTA peaks in the same temperature range where the thermal degradation of the copolymers takes place, crystalline transition (237–272–299°) and melting (299–308–381°), the respective enthalpies being 9.5 and 41.1 cal/g [4]. For evaluation of the DTA peak areas of the polymer degradation a value of 50.6 cal/g was employed, which corresponds to the sum of the two thermal effects of $NaNO_3$.

For the granulometric analysis, 100 g dry polymer powder was screened on a set of sieves with meshes between 60 and 600 nm. The sieves were arranged in order of decreasing sieve mesh dimensions, the sample was put on the sieve with the greatest diameter of the mesh and the sample was then screened for 1 h on a vibrator. The polymer amount on each sieve was weighed and the weight % was calculated.

Results and discussions

The introduction of even a small amount of comonomer into the main chain of a homopolymer affects some of its properties, among which are the thermal behaviour and the appearance of the thermal analysis curves. Such curves for AN/VAc and AN/MS copolymers are presented in Figs 2 and 3, compared to that of PAN in Fig. 1.

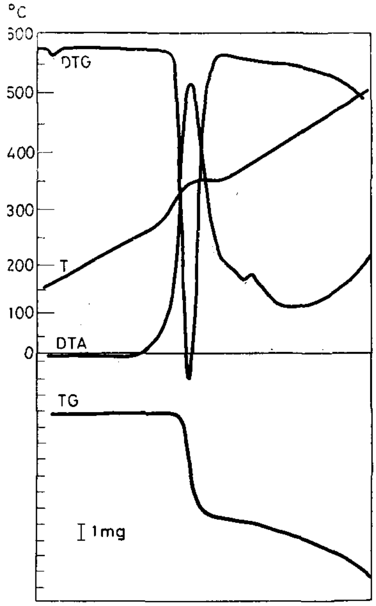

Fig. 1. TG, DTG and DTA curves of polyacrylonitrile

The changes observed depend on both the nature of the comonomer and its content. In the range between 270° and 450° PAN has a single thermogravimetric degradation step (Fig 1), whereas the AN/VAc copolymer (Fig. 2) starting with a content of more than 7% VAc, shows in contrast a second process, much more clearly seen in DTA than in DTG. The thermal effect of this second process is smaller than in the first step so that the degradation rate becomes slower. For AN/MS copolymers, the second degradation process becomes evident at a much smaller concentration of the comonomer. For a concentration of only 10% MS it seems to be more important than the first degradation step; the thermal effect is also larger, so that the decomposition seems overall more rapid in this case (Fig. 3).

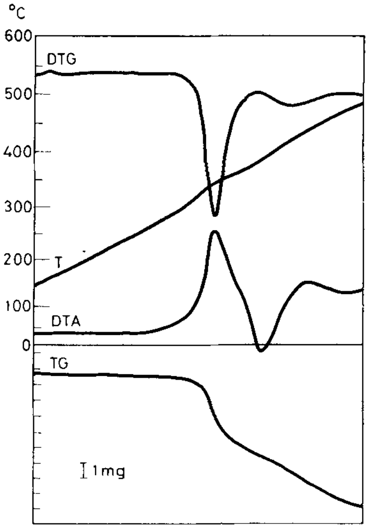

Fig. 2. TG, DTG and DTA curves of binary copolymers (B. C.) with 11.2% VAc

The corresponding DTA curves are very complicated. They consist of a superposition of endo- and exothermic processes which are hard to separate, so that estimation of the heat of reaction becomes quite difficult.

Among the data which can be used for the characterization of the thermogravimetric behaviour under constant working conditions, we may mention the temperatures of each specific stage of degradation, together with the corresponding weight change, the shapes of the DTG and DTA peaks, the reaction heats and the apparent kinetic parameters.

As regards the initial decomposition temperatures (Fig. 4) deduced from both DTA and DTG curves, we find that especially for a comonomer content of more

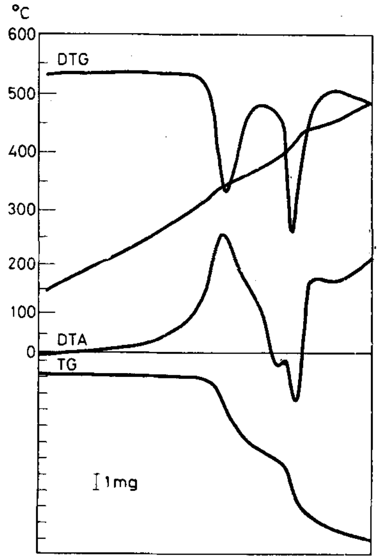

Fig. 3. TG, DTG and DTA curves of binary copolymers (B. C.) with 10% MS

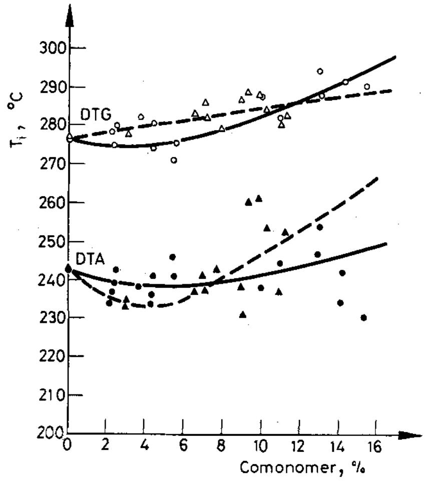

Fig. 4. Dependence of initial temperatures of thermal degradation of the copolymers on the comonomer content. ——— B. C. with MS ●(T_i, DTA); ———○ (T_i,DTG); - - - B. C. with VAc - - △ (filled) (T_i, DTA) - - - - △ (T_i, DTG)

than 5% they show an increasing tendency for both binary studied copolymers suggesting an improvement in thermal stability.

The weight loss in the first degradation process (I) decreases with increasing comonomer content, at the same time the weight loss in the second step (II) increasing. The corresponding change is much more evident for the AN/MS copolymers, as can be seen in Fig. 5. A similar variation to that of the weight loss is displayed by the DTG peaks.

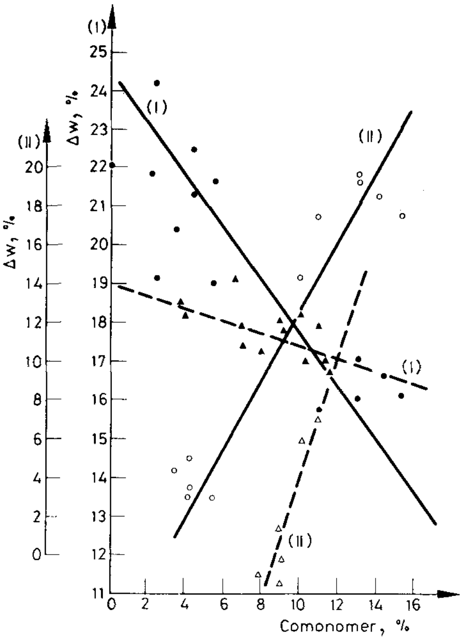

Fig. 5. Dependence of the weight loss in the first (I) and second (II) stage of the degradation on the binary copolymer composition: B. C. with MS ——● stage I ——○ stage II ---- B. C. with VAc --△ (filled) stage I; ---△ stage II

In contrast to the above data, the heat of reaction behaves differently for each of the comonomers. In the case of AN/VAc copolymers, the heat of reaction of the first degradation step shows a minimum at approximately 7% VAc (Fig. 6). The second step is unfortunately less evident in the DTA curves, and because of the high errors in planimetry, the corresponding heats of reaction could not be estimated. In contrast, the heat of reaction of the first step of the degradation of AN/MS copolymers decreases monotonously with the comonomer content. The heat of reaction of the second step (II) increases simultaneously. An accurate determination of the heat of reaction was quite difficult in the range of 9 – 10% MS content, however, because of the complexity of the corresponding DTA curves.

The apparent activation energy, E, of the thermal degradation under constant conditions was calculated according to the Freeman – Carroll [5] method, using a program written in JAL-language for a JEC-5 computer. As shown in Fig. 7, the apparent activation energy for the degradation of the copolymers in air also shows typical trends for the first step as were found in the heat of reaction.

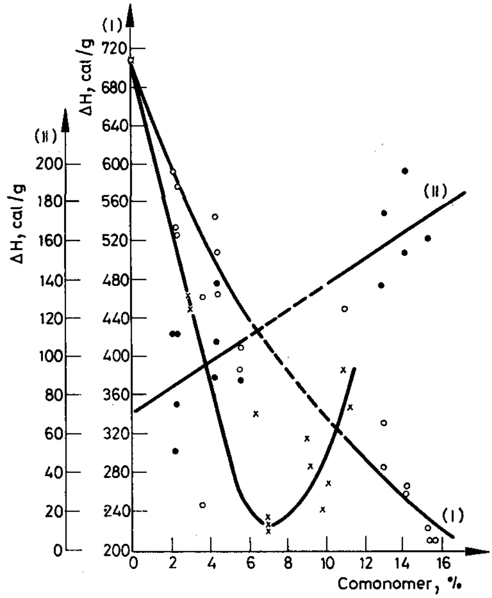

Fig. 6. Dependence of the reaction heat of the thermal degradation in air on the comonomer content of binary copolymers. (x) B. C. with VAc; (○) B. C. with MS I — first stage of the degradation (●) II — second stage of the degradation

This time, however, the AN/VAc copolymers present a maximum of the apparent activation energy at approx. 7% VAc, while the AN/MS copolymers are characterized by important oscillations of this parameter from one sample to another. It seems, however, that the E values decrease with increasing comonomer content. In order to find an acceptable explanation of this apparent discordance between the changes of the characteristic degradation temperatures and of the heat of reaction compared to the apparent activation energy, granulometric analyses of the copolymers were performed. These too showed specific variation, as can be observed in Figs 8 and 9.

From these Figures it is concluded that while for AN/MS copolymers the maximum of the grain distribution shifts to larger values with increasing comonomer content, for AN/VAc copolymers it shifts initially to higher granulation, and then returns to a smaller one as the VAc content increases further. Increasing granulation of the sample could produce a relative decrease in the rate of elimination of the volatile compounds and thereby a corresponding variation of the characteristic temperatures and kinetic parameters, causing a decrease of the apparent activation energy. The observed modifications however, are too big to be explained

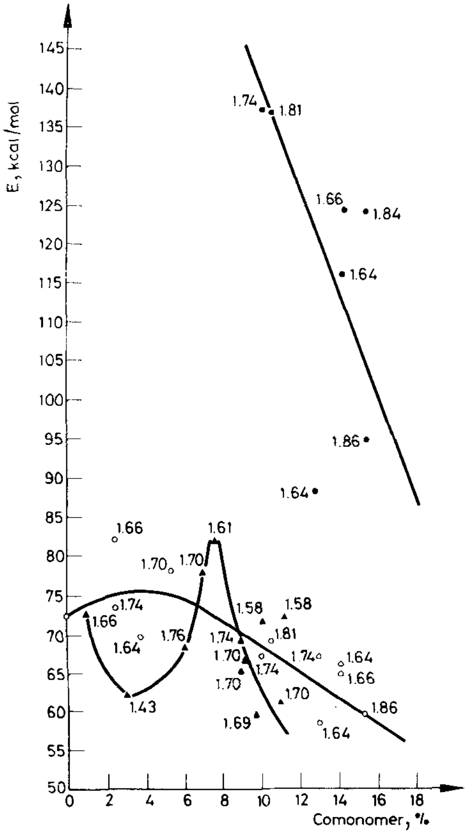

Fig. 7. Dependence of apparent activation energy of the first degradation process in air under constant working conditions on the comonomer content. (△ filled) B. C. with VAc; (○),(●) B. C. with MS (○) (I) first stage of degradation (●) (II) second stage of degradation. The numbers in the Figure represent the values of the relative viscosities

merely by the variation in grain sizes, so that we suggest an influence of the copolymer structure on the thermal behaviour. This hypothesis is supported by the microscopic appearance of the AN/MS copolymers films as presented in Fig. 10, which suggests increasing heterogeneity with increasing MS content.

This suggests an influence of the nature and content of the comonomer on the copolymer superstructure and therefore on the thermal behaviour, since it is known that an increase of the microheterogeneity is always accompanied by a decrease of the thermal stability [6]. In addition, one may presume that introduction of a comonomer into a polymer chain could cause some modification in the degradation mechanism because of the modifications which can occur in the depropagation and chain transfer reactions. Such modifications have been observed in other copolymers [7, 8].

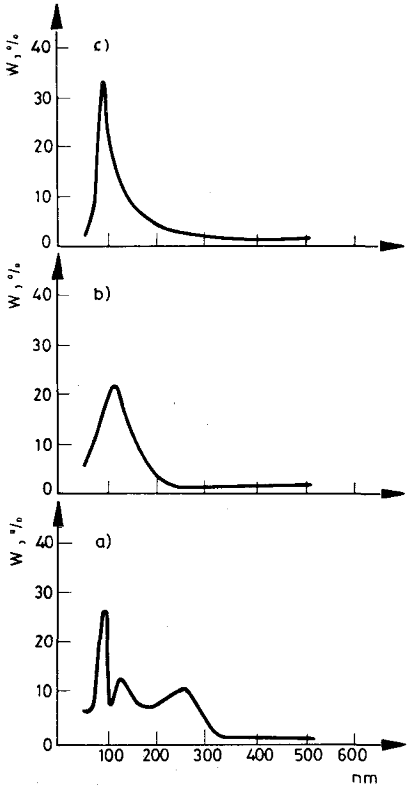

Fig. 8. Granulometric curves of binary copolymers with VAc: a) B. C. with 4.9% VAc; b) B. C. with 10% VAc and c) B. C. with 14.1% VAc

In the case of the binary copolymers with VAc, the minimum of the heat of reaction (Fig. 6) and the maximum of the apparent activation energy (Fig. 7) can be partially caused by the increase of the crystallization index of the studied copolymers in the composition range 7–9% VAc (see the results in the earlier paper [9]), and by the specific variations of the granulosity with the comonomer composition. The films of these copolymers are homogeneous according to microscopic examination.

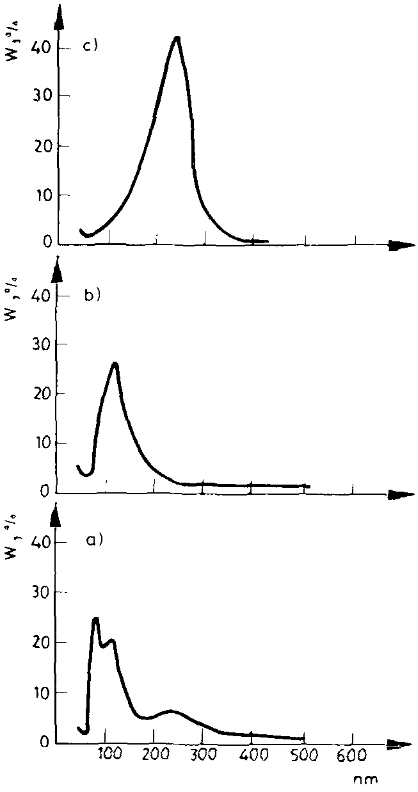

Fig. 9. Granulometric curves of binary copolymers with MS: a) B. C. with 2.2% MS; b) B. C. with 7.4% MS; c) B. C. with 15.3% MS

However, a decisive role will be played by the sequence distribution in the polymer chain, which may influence not only the number of accidental scissions, but also the depropagation zip length, so that an interpretation of the thermal behaviour data of copolymers becomes very complicated.

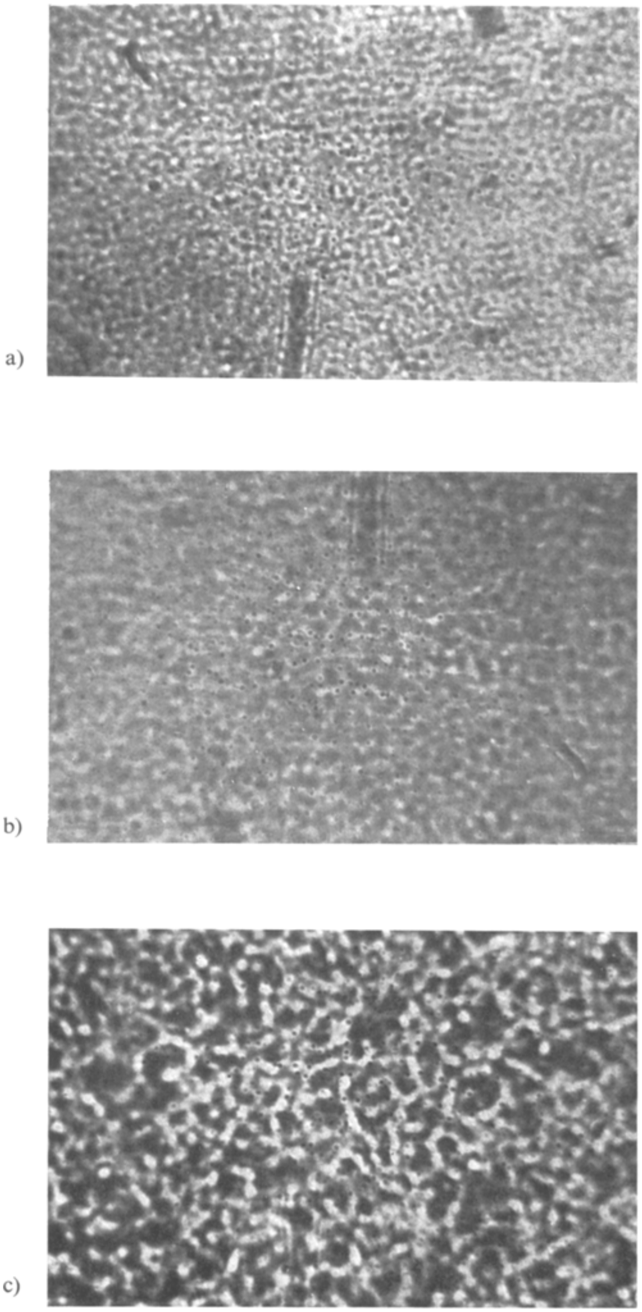

Fig. 10. Microscopic aspect of films of binary copolymers with different contents of MS (magnification 600×, phase contrast) a) 5% MS; b) 30% MS; c) 40% MS

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Résumé — On a étudié l'influence de la nature du copolymère et de sa teneur en comonomère ainsi que celle de la structure supermoléculaire sur le comportement thermique des copolymères binaires de l'acrylonitrile avec le vinylacétate et l'α-méthylstyrène. On a établi une corrélation entre ces résultats et ceux d'études granulométriques et microscopiques.

Zusammenfassung — Der Einfluss der Beschaffenheit und des Comonomergehaltes des Copolymeren, sowie der supermolekularen Struktur auf das thermische Verhalten des binären Vinylacetat- sowie des α-methylstyrolcopolymeren von Acrylnitril wurde untersucht. Die Ergebnisse wurden mit granulometrischen und mikroskopischen Untersuchungen verglichen.

Резюме — Было изучено влияние природы кополимера, содержания в нем мономера и его сверхмолекулярной структуры на термическое поведение бинарных кополимеров винилацетата и α-метилстирола с акрилонитрилом. Полученные результаты коррелируются с гранулометрическими и микроскопическими исследованиями.