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Odd–even effect and thermal stability in series of vinyl polymers.
Part 2. Poly-*n*-alkyl acrylates

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Abstract

Thermal transformations in the series of poly-*n*-alkyl acrylates (PAA) have been studied by mass spectrometric thermal analysis method. Thermal degradation of PAA was shown to proceed via a six-membered transition state of the McLafferty rearrangement type. An odd–even effect in thermal stability of the PAA series depending on the number of methylene units in the alkyl side chain was observed. The electronic reasons for this effect were postulated on the basis of ^{13}C NMR spectroscopy data.

INTRODUCTION

The investigation of polymers of the vinyl series attracts increasing attention because these polymers are being widely used in modern technological processes. These materials have to meet stringent requirements, and this stimulates both the improvement of synthesis procedures and the development of new methods of analysis and quality control of the resulting polymers.

From this viewpoint, the methods of thermal analysis are among the most effective. Therefore, the number of publications dealing with the mechanism of thermal degradation of vinyl polymers is increasing [1–3].

The authors have previously [4] investigated the thermal degradation of poly-4-*n*-alkylstyrenes (PAS) by mass spectrometric thermal analysis (MTA), DTA and TGA and have detected an odd–even effect of thermal stability of PAS which depends on the number of methylene groups in the alkyl substituent. It was shown that this dependence in the PAS series agrees with the changes in the chemical shift on carbon atoms in the

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benzene ring. This fact indicates that the odd–even effect is electronic in nature, and makes it possible to explain the difference in thermal stability in the PAS series from the standpoint of higher or lower stability of radicals generated in the main chain of the polymer.

However, the cause of this effect is still unknown. One of the paths for the solution of this problem is the application of a wider set of polymer samples in which the odd–even effect of thermal stability can be observed.

For this purpose, the representatives of a series of poly-*n*-alkyl acrylates (PAA) ranging from polymethyl acrylate (PAA-1) to poly-*n*-decyl acrylate (PAA-10) have been investigated by MTA and ^{13}C NMR spectroscopy. This investigation showed that the odd–even effect of thermal stability is also manifested in the PAA series. However, in contrast to PAS, for PAA no correlation with the changes in the chemical shift on any carbon atom of the monomer unit is apparent. This stems from the fact that thermal transformations in the PAA series are determined by the relative stability of a six-membered intermediate formed according to a type of McLafferty rearrangement, whereas the initial sample does not contain this intermediate.

EXPERIMENTAL

Poly(alkyl acrylates) from PAA-1 to PAA-7, and PAA-9, were obtained from commercial monomers. These monomers containing hydroquinone as inhibitor were purified by means of a 5% alkali solution. Monomers for PAA-8 and PAA-10, which are not produced commercially, were synthesized by transesterification of methyl methacrylate by an appropriate alcohol in the presence of *p*-toluenesulphonic acid [5].

The polymers PAA-1–PAA-4 were obtained by photostimulated polymerization in a 15% chloroform solution in the presence of 0.1% of benzoyl peroxide at 20°C for 15–20 h.

Polymers PAA-5–PAA-10 were obtained by photostimulated polymerization in a 30% benzene solution in the presence of 0.1% of azobis(isobutyronitrile) at 20°C for 20–40 h.

The resulting polymers were precipitated in a benzene–ethanol system. The intrinsic viscosity of the polymers in toluene varied for different samples from 1.4 to 1.6 dl g^{-1}, which corresponds to $M_w = 10^5$–10^6 Da.

Mass spectrometric thermal analysis was carried out on an MKh 1321A instrument (USSR) at 18 eV by the procedure described in ref. 6 at a heating rate of 6 K min^{-1}. A sample with a mass of 0.1 mg was fixed directly onto the thermocouple with the aid of aluminium foil. The thermocouple was introduced through a Teflon tube directly into the destructor, which greatly increased the precision of temperature measurements.

The ^{13}C NMR spectra were recorded for 10–15% polymer solutions with tetramethylsilane as the internal standard in benzene-d_6 on a Bruker AC 200 instrument (50.3 MHz).

DISCUSSION

In discussing the problems of thermal degradation of polymers, it should be emphasized that degradation itself is a complex multistage process. It consists of a series of consecutive and simultaneous reactions of initiation, depolymerization, scission of the side and main chains of the macromolecules, chain termination, recombination, etc. The process of diffusion of reaction products throughout the sample also plays a certain role. Each of the above reactions is characterized by its own kinetic parameters. Hence, each specific process in each instance has its own individual mechanism depending on a number of factors. The most important of these factors are, first, degradation conditions, which include temperature, heating rate, the atmosphere in which the process occurs, the aggregate state, the sample size, etc. Secondly, certain factors are the specific features of the chemical structure of the sample: various defective units, end groups, impurities, etc. For this reason the results reported by different authors are often different.

Recently, several papers have been published [1–3] in which the authors consider the mechanisms of thermal degradation of polystyrene, poly-4-methylstyrene, and polymethyl methacrylate on the quantitative level. However, it is quite evident that with the present state of our knowledge it is not possible to take into account all above-mentioned factors.

Hence, in this paper we did not attempt to investigate in detail the mechanisms of thermal degradation of PAA but considered only those aspects, related to the problems of degradation initiation, which were necessary for the investigation of the odd–even effect in the study of thermal stability of poly(alkyl acrylates).

Range of PAA thermal transformations and thermal stability criterion

Just as in the investigation of polyalkylstyrenes [4], the temperature of the peak maximum of gaseous product evolution was chosen as the criterion for thermal stability. However, in the case of PAA there are several specific features.

(1) The gas evolution curve is of a bimodal character with maxima in the range of 260–280 and 360–380°C (Fig. 1).

(2) The molecular ion peak is absent in the mass spectra of monomers (with the exception of methyl and ethyl acrylate; Fig. 2), which makes it difficult to interpret the data.

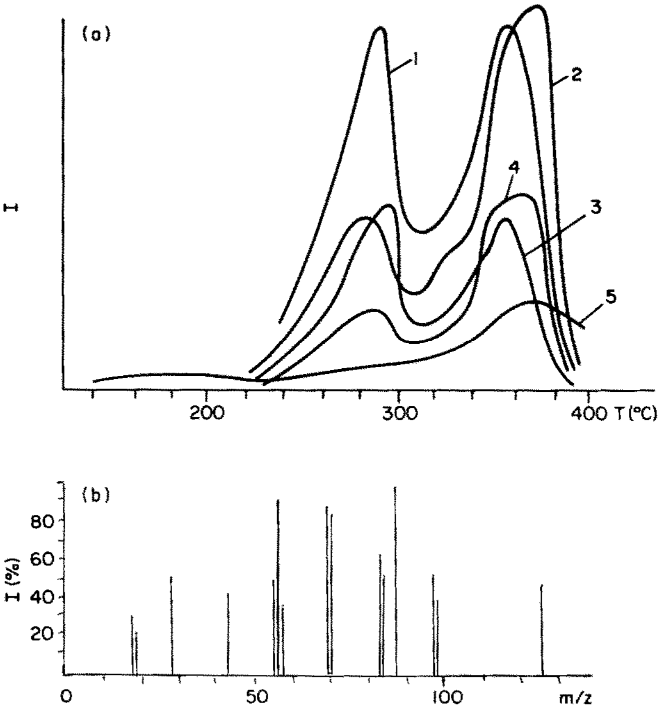


Fig. 1. (a) Dynamics of the intensity change for the main ions in MTA of PAA-9: curve 1, *m/z* 87; curve 2, *m/z* 56; curve 3, *m/z* 126; curve 4, *m/z* 55; curve 5, *m/z* 44; (b) mass spectrom of PAA-9 degradation products at 355°C (18 eV).

(3) In the high-temperature peak of gas evolution, the temperatures of the maximum on the curves of elimination of different products differ slightly (Fig. 1). This is particularly pronounced on the curve of total ion current (Fig. 3) and indicates that the investigated process is very complex.

Hence, three special points may be distinguished on the gas evolution curve: the temperature of the maximum of the low temperature peak and two temperatures of maxima in the range of the high-temperature peak.

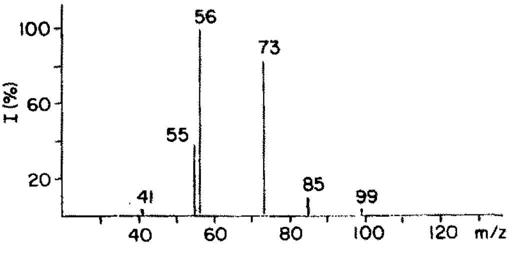


Fig. 2. Mass spectrum of butyl acrylate (18 eV).

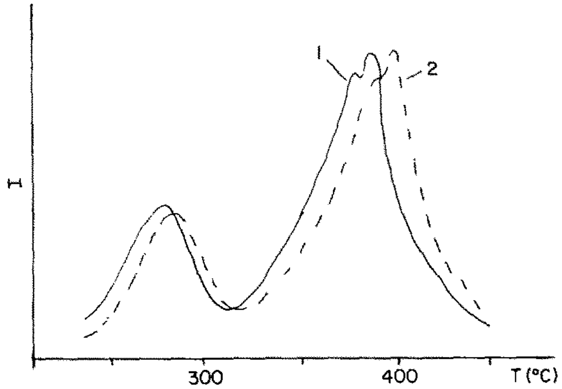
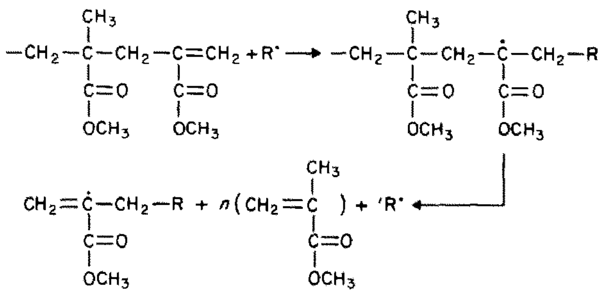


Fig. 3. Total ion current curves for PAA-4: 1, undeuterated polymer; 2, polymer with deuterated alkylene substituent.

In other words, in the case of PAA, at least three paths of development of the thermal degradation processes may be distinguished.

The analysis of mass spectra belonging to the low- and high-temperature peaks shows that the set of the most intense ions is virtually the same. For PAA-9 (Fig. 1) ions with the following *m/z* values can be distinguished: 126 (nonene), 112 (octene), 56 (butene), 70 (pentene), 84 (hexene), 98 (heptene), 18 (water), 28 (carbon oxide and ethylene), 44 (propane and carbon dioxide), etc. However, the intensity ratio of the ions differs for the low- and high-temperature peaks, which may indicate that the destruction mechanisms in these cases are different.

Manring [7], taking as an example polymethyl methacrylate, has convincingly shown that the low-temperature peak of product yield is not formed as a result of the scission of "weak" bonds in the structures of the "head-to-head" type and not as a result of the scission of the C–C bond in the β position to the vinyl end group, but is caused by the transfer of the primary radical to the terminal double bond followed by depolymerization.



$$-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{OCH_3}{|}}{\underset{C=O}{\underset{|}{C}}}}}-CH_2-\underset{\underset{OCH_3}{|}}{\underset{C=O}{\underset{|}{C}}}=CH_2+R^{\cdot}\longrightarrow -CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{OCH_3}{|}}{\underset{C=O}{\underset{|}{C}}}}}-CH_2-\underset{\underset{OCH_3}{|}}{\underset{C=O}{\underset{|}{\dot{C}}}}-CH_2-R$$

$$CH_2=\underset{\underset{OCH_3}{|}}{\underset{C=O}{\underset{|}{\dot{C}}}}-CH_2-R+n(CH_2=\overset{CH_3}{\overset{|}{\underset{\underset{OCH_3}{|}}{\underset{C=O}{\underset{|}{C}}}}})+{}'R^{\cdot}$$

The primary radical R$^{\cdot}$ can be formed as a result of the destruction of weak structures present in the polymer itself, in impurities and so on.

It may be assumed that in the case of PAA the existence of a

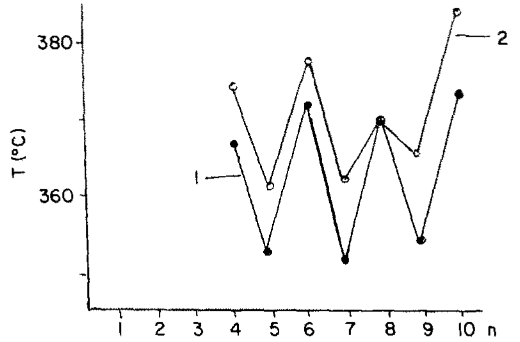


Fig. 4. Dependences of T_{max} and T'_{max} for PAA samples on the number of methylene groups in the alkylene substituents: 1, T_{max}, 2, T'_{max}.

low-temperature peak is also a consequence of the temperature of similar processes, because the temperature of its maximum does not change with the variation in the structure of the monomer unit. The existance of double bonds at the end of the macromolecules is due to the technology of polymer preparation and is not related to the thermal stability of the main structure.

Hence the temperature characteristics of the high-temperature peak should evidently be considered as the criterion for thermal stability. As for the existence of two temperatures of the maximum in the high-temperature peak T_{max} and T'_{max} they agree with each other (Fig. 4) and any of them can be used as the criterion.

Odd–even effect in the PAA series and its electronic nature

Figure 4 shows the dependences of T_{max} and T'_{max} on the structure of monomer units for the PAA series obtained at a heating rate of 6 K min^{-1}. It is clear that, just as for polyalkylstyrenes, alternation of thermal stability in the PAA series depends on whether an odd or an even number of methylene groups is contained in the alkyl substituent. Similarly to polyalkylstyrenes, the "even" representatives of the series exhibit higher thermal stability than the "odd" representatives. However, in contrast to PAS, the odd–even effect in the PAA series is manifested begining only from PAA-4.

We suggest that the electronic nature of the odd–even effect in the PAA series may ultimately be due to the same reasons as for PAS. Figure 5 shows the plots of the dependence of thermal stability and the chemical shift of the C1 atom of the benzene ring, nearest to the main chain, on the number of methylene groups in the alkyl substituents. It is assumed that under these conditions (at a heating rate of 6 K min^{-1}) the reaction

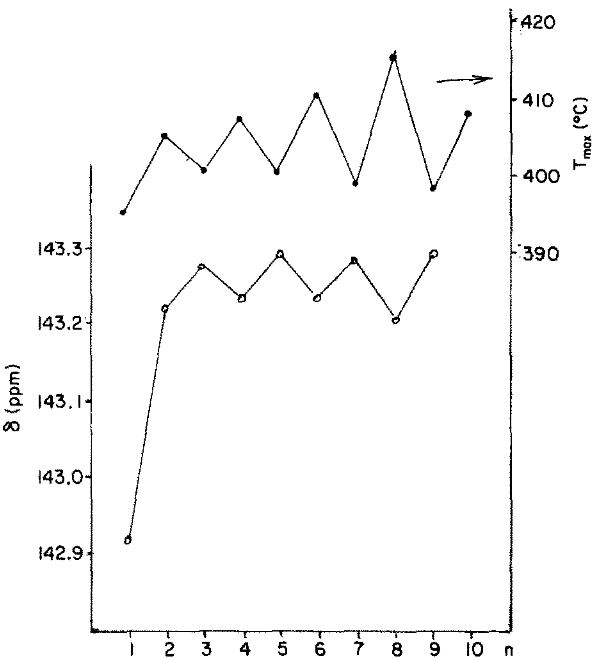
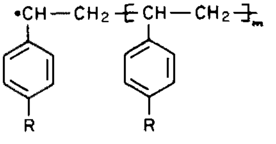


Fig. 5. Plot of T_{max} and chemical shift vs. number of methylene groups for polyalkylstyrene samples.

determining the predominant direction of the degradation mechanism is the scission of the main chain (although at lower heating rates the initiation of depolymerization is related to the scission of alkyl side chains).



Hence, the greater the stability of the radical formed at the chain end the lower is the free energy of this process and, consequently, the lower its temperature. The stability of the polymer radical increases with decreasing electron density on the C1 atom because in this case the coulombic barrier becomes lower and electron delocalization in the aromatic ring is facilitated. Because the charge Q on the atom is related to the chemical shift (C.S.) as follows

$$Q = A - B(\mathrm{C.S.})$$

where A and B are constants, the plots in Fig. 5 evidently confirm this hypothesis.

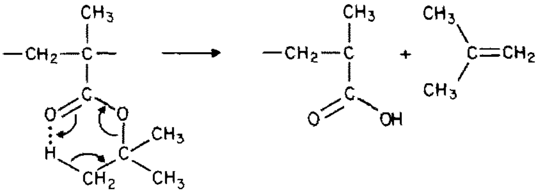
TABLE 1

Chemical shifts on carbon atoms of alkyl substituents in PAA

Polymer	Number of atom									
	1	2	3	4	5	6	7	8	9	10
PAA-4	64.17	30.42	18.92	13.56						
PAA-5	64.50	28.09	27.79	22.15	13.78					
PAA-6	64.50	31.30	28.34	25.32	22.36	13.83				
PAA-7	64.54	31.60	28.86	28.43	25.68	22.46	13.91			
PAA-8	64.55	31.71	29.16	28.46	28.45	25.77	22.51	13.94		
PAA-9	64.55	31.75	29.50	28.94				22.53	13.94	
PAA-10	64.56	31.82	29.53	28.50			28.49	25.77	22.55	13.94

Table 1 gives the data from ^{13}C NMR spectroscopy for the PAA series. The table shows that, in contrast to PAS, for the PAA series no direct correlation is observed between the C.S. on any carbon atom of the polymer molecule and the thermal stability of the sample. However, such a correlation can be detected if it is not the dependence of the absolute values of C.S. that is considered, but their difference $\delta_{3,4}$ on the C3 and C4 atoms of the alkyl substituent (Fig. 6). It is natural that all these considerations refer to polymers in which the length of the alkyl chain exceeds four methylene groups.

In our opinion, the reason for this phenomenon is the fact that esters in general and their thermal transformations in particular are characterized by the tendency to formation of a six-membered transition state. An example of this effect is provided by the well-known McLafferty rearrangement [8]. For poly(alkyl methacrylates) with a branched alkyl chain, this mechanism is widely recognized [9]. In the case of poly(*tert*-butyl methacrylate), this mechanism is observed at a relatively low temperature (180–220°C). As a result, an olefin and a polyacid are formed.



The degradation of other polymethacrylates in which the number of hydrogen atoms at β-carbon exceeds five proceeds by the same mechanism and almost equally easily. It is considered in the case of PAA with a normal alkyl chain that this process does not occur at low temperatures [9].

It may be assumed that at high temperatures the tendency to the

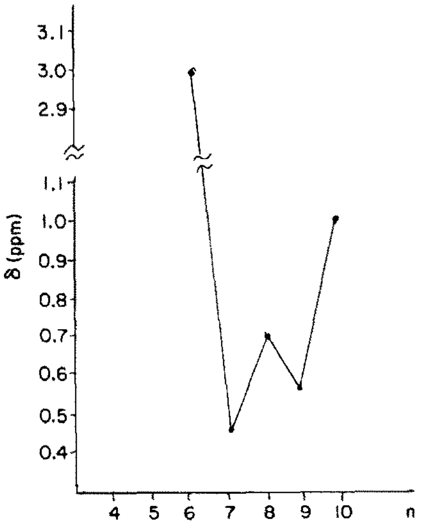
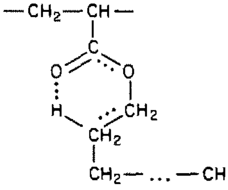


Fig. 6. Value of $\delta_{3,4}$ vs. number of methylene groups for PAA samples.

formation of a six-membered transition state is also sufficiently high for



poly(n-alkyl acrylates) with unbranched alkyl groups. The cyclic intermediate is absent in the initial polymer, and therefore a direct alternation of chemical shift at any atom of the monomer unit is absent in the ^{13}C NMR spectra.

The value of $\delta_{3,4}$ indicates that the C3–C4 bond is polar. The polarity of this bond affects the "screening" of the induction effect. We believe that this "screening" influences the ability of hydrogen at the C2 atom to form a hydrogen bond with the carbonyl oxygen atom of the ester group, and facilitates the formation of the cyclic intermediate.

This, in turn, is the starting mechanism of PAA thermal degradation. Because of redistribution of electron density, the cyclic structure of the intermediate acquires a partial π-character, and it may be assumed that in this case mechanisms similar to those observed in polyalkylstyrenes exist (if the cyclic intermediate is considered to be a remote analogue of the aromatic ring in PAS).

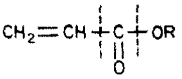
In this intermediate, the side alkyl group contains two methylene units fewer than the corresponding polyalkylstyrene because the two first units are contained in the cyclic intermediate.

The six-membered intermediate formed is stabilized by conjugated bonds and, in our opinion, is relatively stable. In other words, the rate constant for its formation is comparable with that for its degradation.

Hence, in considering the degradation mechanism the probabilities of the occurence of both these reactions should be taken into account. In this case factors determining both the facility of intermediate formation (polarization of the C3–C4 bond) and polymer degradation by the depolymerization mechanism (charge alternation on the carbon atom nearest to the main chain) seem to act in the same direction, thus increasing the effect of thermal stability alternation.

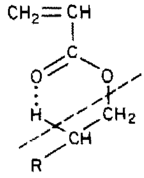
In our opinion, the manifestation of the effect of electron density alternation depending on the odd or even number of methylene groups in the alkyl substituent is related to a change in the symmetry of the wave functions at boundary atoms separating the parts of the polymer with different types of wave functions. The "boundary effects" should be increasingly manifested with increasing difference in the character of wave functions in these polymer moieties. In the case of PAS they may be the π-orbitals of the benzene ring and the σ-orbitals of the alkyl group. In the case of PAA, the symmetries of the wave functions of the ester group and the alkyl substituent differ from each other to a much lesser extent than for PAS. Hence, the odd–even effect of charge change on carbon atoms in PAA is not apparent.

Since we consider that the cyclic intermediate can initiate PAA degradation by a mechanism similar to that for PAS, the degradation products should contain the monomer. However, the mass spectra of the monomers (alkyl acrylates) (Fig. 2) do not contain a peak corresponding to the molecular ion. This is because of the easy α- and β-fragmentation of the monomer by the influence of energy over a wide range (temperature or electron impact). As a result, olefins, acids, alcohols and the like are formed [7, 10].



$\mathrm{CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}OR}$

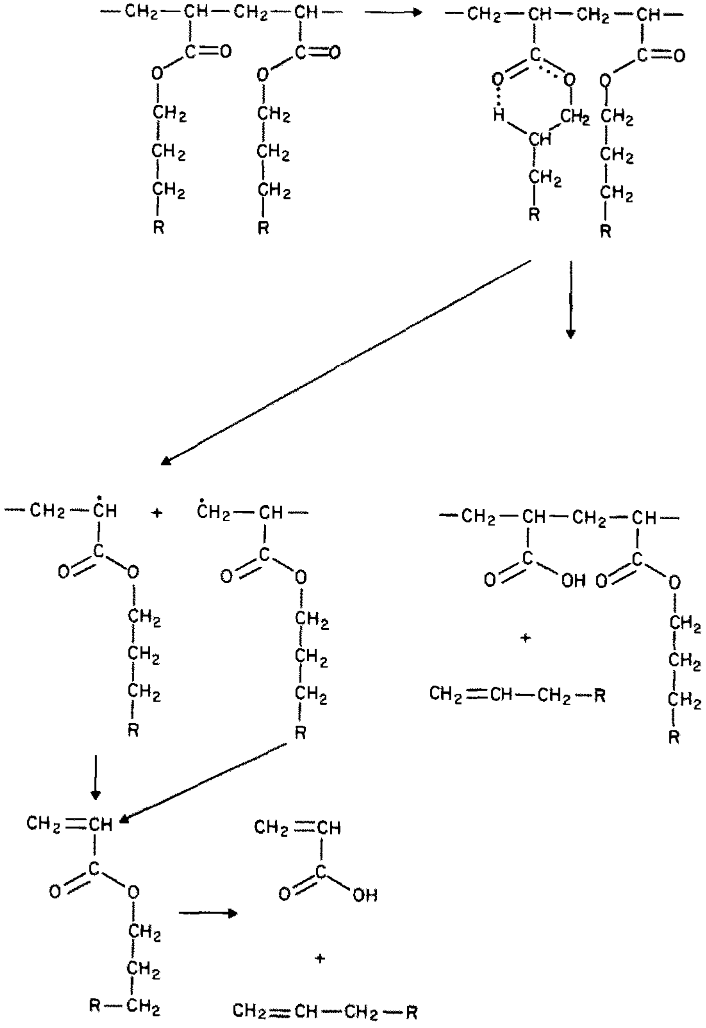
α-scission



β-scission
McLafferty
type reaction

Because two temperatures of the maximum corresponding to the yield of products with different masses may be singled out on gas evolution curves in the range of the high-temperature peak (Figs 1 and 3), it may be concluded that at least two processes occur in this temperature range. The mass spectrum of the degradation products is a superimposition of the spectra of several products. Hence, the analysis of the mass spectrum does not allow us to draw a conclusion about the presence of the monomer in the degradation products and makes it difficult to interpret the results. For the solution of this problem we are planning to carry out chromatomass spectrometric experiments and to use field-ionization mass spectrometry.

As for the specific mechanisms of these two degradation paths, since both temperatures, T_{max} and T'_{max}, agree with each other, they are evidently determined by the existance of a common initial stage. We consider it to be the stage of the cyclic intermediate. The fact that in the initial stage the alkyl substituent directly participates in the process is confirmed by the isotropic effect: T_{max} and T'_{max} for PAA-4 in which all hydrogen atoms in the alkyl group have been replaced by deuterium are 10 degrees higher than for the non-deuterated analogue (Fig. 3). The cyclic intermediate can give rise to two processes (see scheme below): main chain scission with subsequent depolymerization, and β-degradation.



In the former case the monomer is formed and can subsequently be decomposed to acrylic acid and alkene. In the latter case, alkene is abstracted directly from the polymer. These processes can give rise to other reactions, the products of which have already been described [10].

We are well aware of the fact that this scheme of initiation of PAA degradation does not reflect the entire complexity of the processes of chain mechanism initiation, but represents only the first attempts to describe the process of polymer degradation. However, the detection of the odd–even effect of thermal stability for the PAA series has not only permitted us to draw certain conclusions about the main features of the degradation mechanism, but has also shown that a similar effect to that already described for the polyalkylstyrene series is not exceptional: it reflects certain relationships of thermal degradation of vinyl series polymers.

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