Thermochimica Acta, 186 (1991) 19–34
Elsevier Science Publishers B.V., Amsterdam

Odd–even effect and thermal stability in the series of vinyl polymers.
Part 1. Poly-4-*n*-alkylstyrenes

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(Received 20 November 1990)

Abstract

Thermal transformations in the poly-4-*n*-alkylstyrene (PAS) series (from poly-4-methylstyrene to poly-4-*n*-decylstyrene) have been studied with the aid of mass-spectrometric analysis, differential scanning calorimetry and thermogravimetric analysis. In the investigation of chemical properties of polymers, an odd–even effect of the thermal stability of poly-4-*n*-alkylstyrene, depending on the number of methylene groups in the alkyl substituent, was detected. It was shown that the odd–even effect is of electronic nature. The agreement between the thermal stability of polymers and the chemical shift on carbon atoms in the benzene ring and the alkyl substituent was established with the aid of ^{13}C NMR spectroscopy. It was established that the character of the dependence of thermal stability on PAS structure varies with the conditions of analysis, in particular, with the heating rate and the medium, owing to change in the mechanisms for thermal degradation of the polymers.

INTRODUCTION

The investigation of poly-4-alkylstyrenes (PAS) is of interest with respect to both the preparation of new polymer materials and the study of theoretical aspects of thermal degradation and thermal stability of polymers.

In recent years, polymers based on PAS have begun to be used in practice. Thus, organic glasses obtained from these polymers exhibit higher thermal characteristics than those of previously known organic glasses [1], and it is proposed to use compositions containing 4-methylstyrene in the production of video and audio disks and disks for the recording, storage and reproduction of information with the application of laser procedures [2].

In a number of papers, the mechanism of thermal transformations of poly-4-methylstyrene (PAS-1) has been investigated under conditions of isothermal heating in a closed volume [3–5]. It has been established that, in contrast to polystyrene (PS), PAS-1 is characterized by a tendency towards crosslinking as a result of chain transfer to the *p*-methyl group, with the subsequent formation of a three-dimensional network. Upon prolonged heating, one can observe competition between the formation of a crosslinked gel and the degradation of the uncrosslinking polymer. Moreover, the specific contribution of each of those processes depends on the temperature [4,5]. Similar crosslinking processes have been detected for poly-4-ethylstyrene and poly-4-isopropylstyrene but have not been observed for poly-4-tert-butylstyrene, in which no hydrogen atom is present at the first carbon atom of the alkyl chain [3].

It may be assumed that this tendency of PAS towards the formation of a three-dimensional network will greatly extend the possibilities of practical application of these polymers as compared with polystyrene. In particular, this peculiarity of PAS will make it possible to change over a wide range the structural and optical homogeneity of products based on this class of polymer.

In the present paper, the thermal behavior of the PAS series ranging from poly-4-methylstyrene to poly-4-*n*-decylstyrene (PAS-10) was investigated with the following aims:

(1) to establish the temperature ranges in which thermal transformations of these polymers take place;

(2) to compare the thermal stability of PS and PAS and to determine the order of thermal stability in the investigated series;

(3) to carry out initial investigations of the mechanism of thermal transformations of polymers and the dependence of this mechanism on the conditions of thermal treatment, in particular the heating rate;

(4) to establish new relationships which make it possible to develop general concepts of the mechanism of thermal degradation of polymers.

The thermal transformations of PAS were investigated with the aid of mass-spectrometric thermal analysis (MTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under the conditions of dynamic heating. This made it possible not only to supplement the picture of the mechanism of the thermal degradation of PAS but also to establish a new odd–even effect of thermal stability in the PAS series and the electronic nature of this phenomenon.

EXPERIMENTAL

The polymerization of 4-alkylstyrenes was carried out on bulk samples in an atmosphere of helium in the presence of 0.2% of benzoyl peroxide at 70 °C for 20–40 h.

The intrinsic viscosity of polymers in toluene varies (depending on the sample) from 0.5 to 0.9 dl g^{-1}, $M_w = 5 \times 10^5–10^6$ [6].

The thermal degradation of PAS by the MTA method was carried out by two procedures. In the first case MTA was carried out with MKh 1320 and MKh 1321A (USSR) instruments. The essence of the procedure is the plotting of the dynamics of evolution of gaseous products during non-isothermal heating of the sample at a constant rate [7]. Two rates were used: 0.5 and 6 K min^{-1}. A sample with a mass of about 0.1 mg was fixed with the aid of aluminium foil directly on the thermocouple, which was introduced through a Teflon seal inside the destructor, which greatly increased the precision of temperature measurements. The mass spectra of the products (at an energy of ionizing electrons of 70 eV) were recorded at intervals of 1 minute with a heating rate of 6 K min^{-1} and at intervals of 3 minutes with a rate of 0.5 K min.

In the second method, a Kratos MS 80 instrument was used. According to this method, a sample with a mass of about 0.1 mg was placed directly in the ion source of the mass spectrometer and heated at a rate of 50 K min^{-1} to a temperature of 400 °C. The information was processed with a Hewlett-Packard computer, and the dynamics of changes in the total ion current were recorded. This reflects the overall process of gas evolution, and the normalized mass spectrum obtained at an energy of ionizing electrons of 70 or 10 eV was recorded every 3 s.

The first method was mainly applied to the study of the kinetics of the yield of gaseous products, whereas the second method was used for analysis of the qualitative composition of the compounds evolved.

The results for TGA and DSC were obtained with a Mettler-3000 thermoanalyzer at a heating rate of 6 K min^{-1} in a nitrogen flow. In the case of TGA, the feed was 5–6 mg, and for DSC it was 2–3 mg.

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

DISCUSSION

In the present paper relatively fine temperature effects were investigated in some cases; thus it was necessary to choose the criterion of thermal stability corresponding to this problem. This, in turn, requires the knowledge of details of the mechanism for thermal transformations of PAS under the experimental conditions.

Temperature ranges of PAS transformations and the main features of the mechanism for thermal degradation

Under the condition of MTA with dynamic heating under a vacuum of 10^{-5}–10^{-6} Pa, in contrast to isothermal heating in a closed volume, all the polymer is finally converted into gaseous products. At a heating rate of 50 K min^{-1}, curves of the total ion current were obtained exhibiting two temperature ranges in which gaseous products are evolved (Fig. 1, curve 1): from 150–300 °C and from 300 °C upwards. It can be seen that the main mass of the products is evolved in the second range. However, if the polymer is

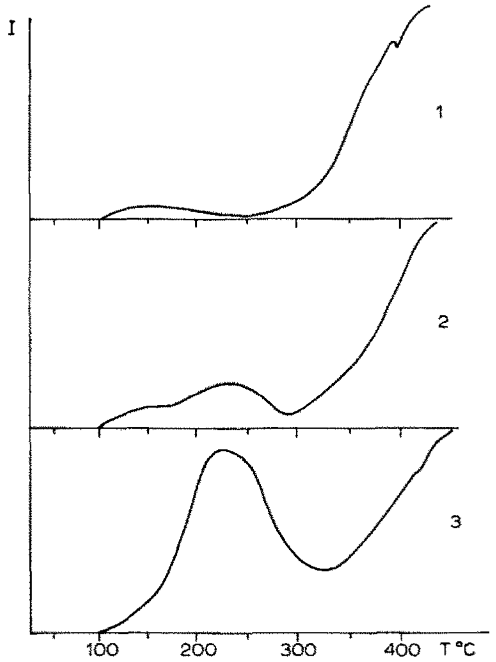


Fig. 1. Total ion current curves during MTA runs (50 K min^{-1}) for: 1, unheated PAS-4; 2, PAS-4 heated to 300 °C for 20 h; 3, PAS-4 heated to 300 °C for 40 h.

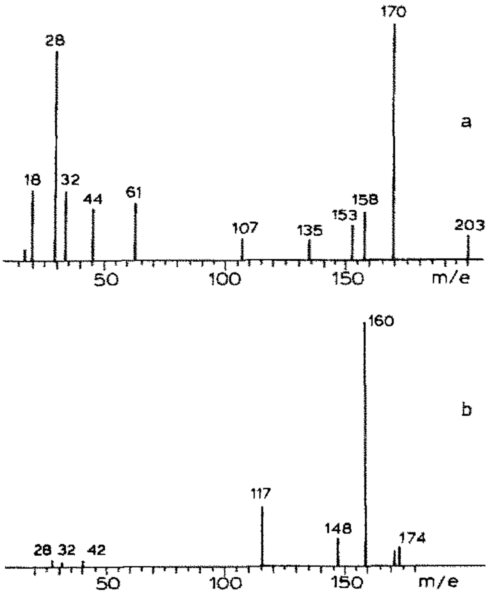


Fig. 2. Mass spectra of compounds formed during MTA of unheated sample of PAS-4 (energy of ionizing electrons 10 eV): a, at 200 °C; b, at 400 °C.

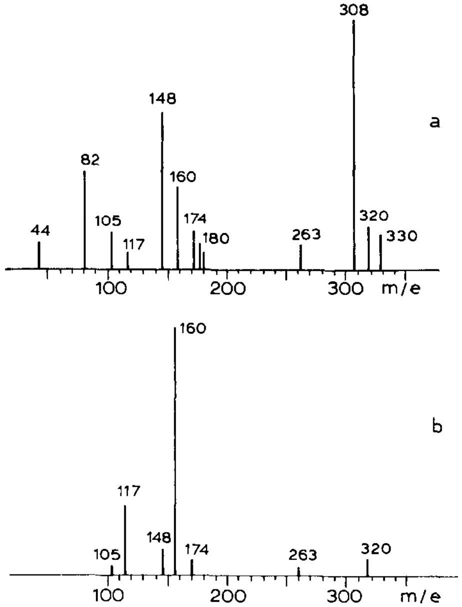
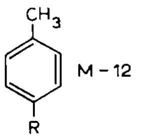
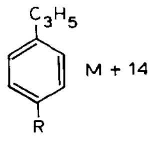


Fig. 3. Mass spectra of compounds formed during MTA of PAS-4 sample heated to 300 °C for 40 h (energy of ionizing electrons 10 eV): a, at 200 °C; b, at 400 °C.

previously heated in a closed volume under dynamic conditions up to 300 °C for 20 or 40 h (Fig. 1, curves 2 and 3 respectively), the ion current in the low temperature range increases. The analysis of the mass spectra of the products (Fig. 2) indicates that, in an unheated sample in the low temperature range, ions with a mass of 17, 18, 28 and 44 (oxygen-containing compounds) and with a mass of 170 (diphenyl oxide) are detected but products of depolymerization are absent. In contrast, in the high temperature range, mainly the monomer is present, i.e. the main process is depolymerization.

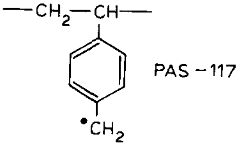
In a polymer previously heated to 300 °C in the low temperature range, products of disproportionation with masses of M-12 and M + 14 (Fig. 3) appear. They correspond to the structures



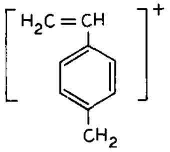


The reason for this disproportionation may be the degradation of defective polymer units formed as a result of the attachment of monomers according to the "head-to-head" type. They are formed during free-radical polymerization and as a result of recombination of macroradicals. Their generation in the PAS mass at a high temperature results from the rupture of weak (peroxide) bonds and subsequent processes of chain development and transfer [8].

It also follows from the literature [4,5] that one of the possible paths of thermal degradation of PAS-1 is the formation of macroradicals of the benzyl type



These suggestions are also confirmed by the results of our investigations: the most intense ion in the mass spectra of compounds generated during the decomposition process of all PAS without exception is the ion with a mass of 117, corresponding to a fragmentary ion with the structure



This fact shows that this ion is very stable (resonance stabilized) compared with other possible structures. In this connection, it may be assumed that the thermal degradation of the polymer proceeds by a mechanism analogous to the fragmentation of monomers upon electron impact.

The macroradicals of PAS-117 can recombine with the formation of a crosslinked structure. This is indicated by the presence of ions with masses of 180 and 182 (Fig. 3), which correspond to the structure of diphenylethane. The recombination of macroradicals may also lead to the formation of an alkylstyrene structure differing from the initial structure. Finally, these and other stable macroradicals (e.g., tertiary macroradicals) initiate depolymerization, which proceeds in the second high-temperature range.

All PAS and PS were analyzed by the MTA method at the heating rates 0.5 and 6 K min^{-1}. The time of existence of the polymers in the low-temperature range of thermal transformations at a rate of 0.5 K min^{-1} is about 3.5 h, and at 6 K min^{-1} it is 12 times lower. The fact that in the first case the transformations in the low-temperature range are more profound can be seen from the activation energy of depolymerization. Upon slow heating, the PAS samples are more crosslinked, and for all samples the calculated activation energy is higher by about 5 kcal mol^{-1} than at a heating rate of 6 K min^{-1} (Fig. 4).

Criterion of thermal stability

There are several methods for the evaluation of the thermal stability of polymers. The widespread method of determination of thermal stability

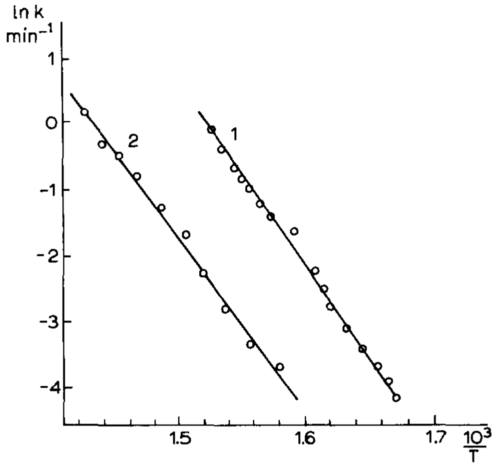


Fig. 4. Dependence of ln k on $1/T$ in the depolymerization of PAS-10: 1, at a heating rate of 0.5 K min^{-1}; 2, at a heating rate of 6 K min^{-1}.

from the initial portions of thermoanalytical curves (e.g., the determination of the start of weight loss in thermogravimetric analysis) does not seem suitable and informative in this case. First, it is characterized by low precision (it is difficult to find the beginning of the exponential function). Second, this method is of interest for practical purposes but does not provide information on the transformations of the main polymer structure because the initial parts of thermoanalytical curves characterize the presence of defective structures, weak bonds, etc. and reflect to a considerable extent the technological features of sample preparation. This, in particular, can be observed by taking as an example heated and unheated PAS samples (Fig. 1).

In this work, thermal stability was determined from the temperature of the maximum rate of PAS depolymerization (temperature of the peak maximum on differential curves). This criterion reflects the scission of the main polymer structure and may be measured with high precision ($\pm 1°$C). This fact is of fundamental importance in the present work in the recording of small temperature effects. Moreover, the maximum temperature is an implicit function of the activation energy, the pre-exponential factor and the heating rate, which follows from the main kinetic equations ($dC/dt = kC^n$; $k = A\ e^{-E_a/RT}$; $T = vt$). For instance, for the first-order kinetics we have $A\ e^{E_a/RT_{max}} - E_a v/RT_{max}^2 = 0$. Hence, the temperature of the peak maximum should be regarded as a kinetic parameter reflecting the mechanism of the process.

Consequently, in the case of MTA, the criterion of thermal stability is taken to be the temperature of the maximum (T_{max}) on the curve of the temperature dependence of the intensity of the molecular ion of the corre-

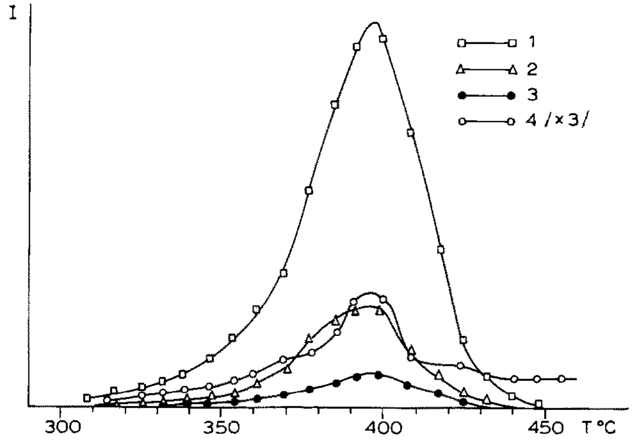


Fig. 5. Dynamics of the intensity change for the main ions in MTA of PAS-6 sample at a heating rate of 6 K min^{-1} in high temperature range (energy of ionizing electrons 70 eV): 1, *m/z* 117; 2, molecular ion *m/z* 188; 3, *m/z* 131; 4, *m/z* 91.

sponding PAS monomer (Fig. 5), and for DSC and TGA this is the maximum temperature on the differential curves in the high-temperature range of thermal transformations (Fig. 6).

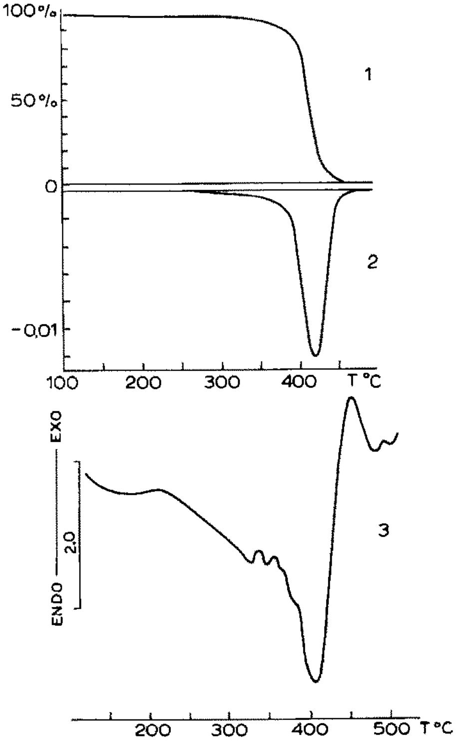


Fig. 6. Thermoanalytical curves for PAS-4 sample (heating rate, 6 K min^{-1}): 1, TGA; 2, DTG; 3, DSC.

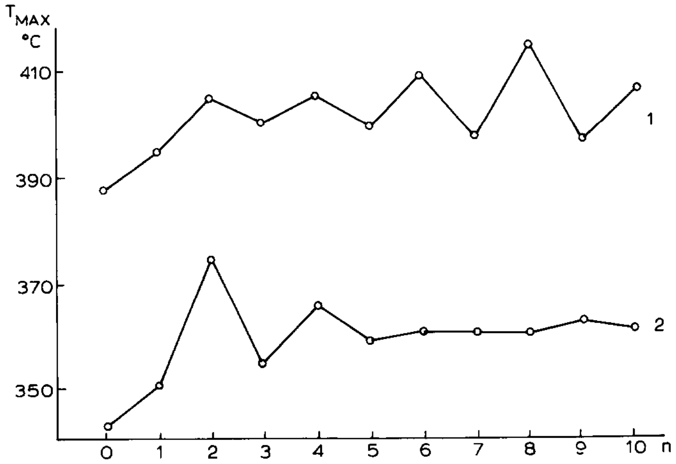


Fig. 7. Dependence of T_{max} on the number of methylene groups in the alkylene substituent for PAS samples obtained in MTA: 1, at a heating rate of 6 K min^{-1}; 2, at a heating rate of 0.5 K min^{-1}.

Thermal stability of PAS and odd–even effect

Before discussing in detail the dependence of PAS thermal stability on the structure of the alkyl substituent and the heating rate, it should be mentioned that an increase in the heating rate leads to a considerable change in T_{max} for all polymers, which, as has been noted before, is a peculiarity of the non-isothermal kinetics. Thus, for PS, the thermal degradation of which is not accompanied by the formation of crosslinks, T_{max} is equal to 343°C in the case of heating at a rate of 0.5 K min^{-1}, and with heating at 6 K min^{-1} it is 388°C.

The first conclusion that may be drawn on the basis of the measurement of T_{max} is the higher thermal stability of the PAS series as compared with PS, regardless of the heating rate (Fig. 7).

When PAS is heated at a rate of 6 K min^{-1} (Fig. 7, curve 1), according to MTA data, an alternation of thermal stability along the entire polymer series can be observed, depending on the odd or even number of methylene groups in the alkyl substituent. In this case all "even" polymers exhibit a higher T_{max} than "odd" polymers, PAS-8 being the most thermally stable of them (T_{max} = 415°C) and PAS-1 exhibiting the lowest stability (T_{max} = 395°C).

Figure 7, curve 2, shows also the dependence of thermal stability of polymers on the structure of the alkyl substituents, and was obtained by MTA at a heating rate of 0.5 K min^{-1}. The first members of the series, just as at a heating rate of 6 K min^{-1}, are characterized by marked variations in the thermal stability, with maxima for "even" polymers and minima for "odd" polymers. These variations are observed from PAS-1 to PAS-4, and

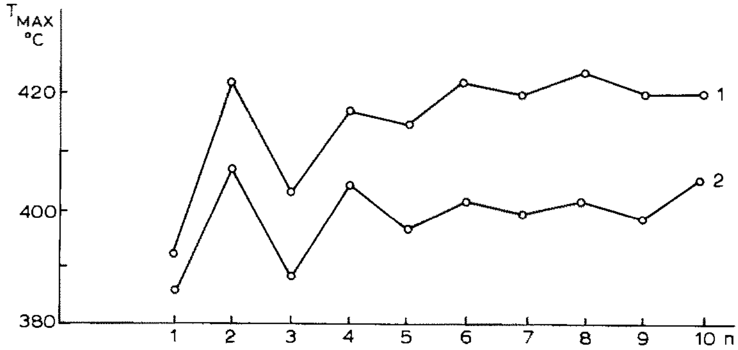


Fig. 8. Dependence of T_{max} on the number of methylene groups for PAS samples obtained by: 1, DTG; 2, DSC.

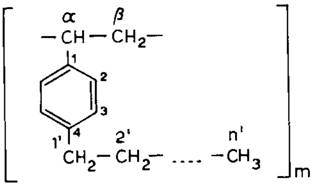
subsequently the curve becomes flatter and is maintained at a level of 360 °C, which is 17 °C higher than for PS. The maximum difference between PAS and PS is observed for PAS-2 (T_{max} = 375 °C) and is 32 °C.

Figure 8 shows the thermal stability curves for the investigated series obtained by DSC and DTG at a heating rate of 6 K min^{-1}. It can be seen that these dependences differ slightly from a similar MTA curve at a heating rate of 6 K min^{-1}. They are characterized by distinct alternation of thermal stability for the first four members of the series, and by less evident alternation for the following members.

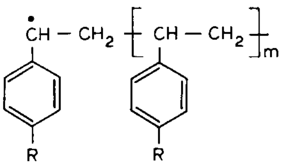
Hence, as a result of the choice of a non-traditional criterion for thermal stability and an increase in the experimental precision, a new effect for polymers, the odd–even effect of thermal stability, was established, taking PAS as an example.

Electronic nature of the odd–even effect and its manifestation in the thermal stability of the PAS series

Further consideration of PAS behavior should begin from an explanation of the higher thermal stability of polymers of this series as compared with that of PS. Note that this fact cannot be explained only by the tendency of PAS to undergo crosslinking, because even in the case of fast heating (6 K min^{-1}), when the probability of crosslinking is low, the difference between the thermal stabilities of PAS-8 and PS is 27 °C. This difference may be associated with the peculiar features of the electronic structure of the polymer and macroradicals. In fact, the ^{13}C NMR data confirm this assumption. The results of PAS investigation by ^{13}C NMR spectroscopy are given in Table 1. The signals of atoms 2 and 3 are closed by those of the solvent (broad peak at 128 ppm).



PAS samples are atactic [6], and hence the signal of the β-carbon atom is broad. The signals of atoms 1 and 4 in PAS-10 cannot be precisely singled out from the background noise, and therfore this polymer is not listed in Table 1. The value of chemical shift (CS) is known to be proportional to the electron density on the corresponding carbon atom (CS increases with decreasing electron density) [9]. Because under these conditions the thermal degradation of PS and PAS proceeds by the depolymerization mechanism its rate is determined by the number of generated radical centers, and it may be expected that, the more stable is the radical formed at the chain end the lower is the free energy of this process, and hence the lower is the temperature at which it will proceed. The lower the electron density at atom 1, the higher the stability of the polymer radical, which favors electron delocalization. For PS, the electron density of atom 1 is lower than for all PAS because the value of CS is 146.4 [10]. Hence, the higher thermal stability of PAS than of PS is due to the destabilizing influence of the alkyl substituent, exhibiting a positive inductive effect on the radical (*).



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The most important result obtained in this work and requiring explanation is the alternation of the thermal stability of PAS depending on the number of methylene groups in the alkyl radical. The odd–even effect of physical properties (e.g. the melting temperature and the temperature of isotropization of liquid crystalline (LC) compounds) of both polymers and low molecular weight compounds, depending on the number of methylene groups in the alkylene fragment, is well known [11]. It is usually considered to be associated with conformational differences in the alkylene fragment containing an odd or even number of carbon atoms [12], which leads to corresponding changes in physical macroproperties. However, a number of properties, e.g. the odd–even effect in the change in the types of the mesophase of LC compounds, cannot be explained by using this approach. Zuev has suggested [13] that, in the series of alkylene–aromatic LC polymers, when the number of methylene groups in the alkylene fragment

TABLE 1

Data from ^{13}C NMR for polyalkylstyrenes depending on the number of methylene groups in alkyl substituents

C	*n*									
	0	1	2	3	4	5	6	7	8	9
	40.8	40.62	40.66	40.66	40.74	40.80	40.80	40.70	40.77	40.76
1	146.4	142.92	143.22	143.28	143.23	143.29	143.23	143.28	143.20	143.29
4	126.2	134.92	141.41	139.81	140.07	140.16	140.06	140.13	140.13	140.14
1′		21.13	28.89	38.10	35.79	35.10	36.20	36.21	36.22	36.17
n'		21.13	16.01	14.12	14.27	14.36	14.41	14.41	14.39	14.39
$n'-1$		–	28.89	25.03	22.85	23.02	23.12	23.15	23.15	23.10

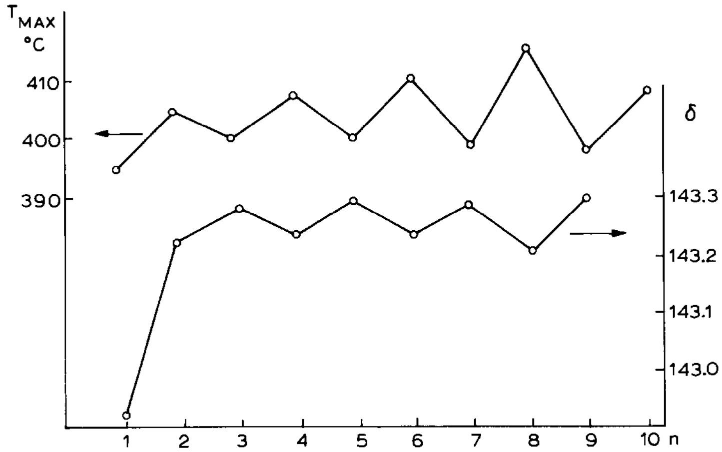

Fig. 9. Chemical shift of C1 atom obtained by ^{13}C NMR spectroscopy and T_{max} obtained by MTA at a heating rate of 6 K min^{-1}, vs. number of methylene groups in PAS samples.

changes, a change in the distribution of electron density takes place both in the alkylene fragment and in the neighboring parts of the chain. These changes obey the odd–even effect and may be one of the factors, apart from the conformational changes, causing the odd–even effect of macroproperties. The odd–even effect in the distribution of electron density has been detected for the series of aromatic LC polyethers with the aid of ^{13}C NMR spectroscopy [14] and UV and CD spectroscopy [15]. However, it was difficult to establish clearly the effect of electronic density distribution on such macroproperties of polymers as, e.g., the melting temperature. Hence, the participation of this factor in the odd–even effect may raise doubts.

It is known that electronic factors are usually more distinctly manifested in the chemical properties of polymers and, in particular, in their thermal stability. It should be noted that, in the investigations of thermal stability in the range of high temperatures, the conformational properties of alkylene fragments are leveled off, and the distribution of electron density does not change greatly, which makes it possible to separate the effects of the above factors.

Figure 9 shows the curves of the dependence of the thermal stability of PAS at a heating rate of 6 K min^{-1} and of changes in CS for carbon atom 1 of PAS on the length of the alkyl substituent. It is clear that the value of CS and, hence, the electron density on atom 1 and the thermal stability measured from T_{max} alternate depending on the number of methylene units in the alkyl fragments. Moreover, the CS of the signal of atom 1 is lower and T_{max} is higher for "even" representatives of the PAS series. Furthermore, even small changes in CS occurring with change in the length of the alkyl radical are well correlated with T_{max}. Thus, the maximum thermal stability is observed for PAS-8, and it is also characterized by the minimum value of

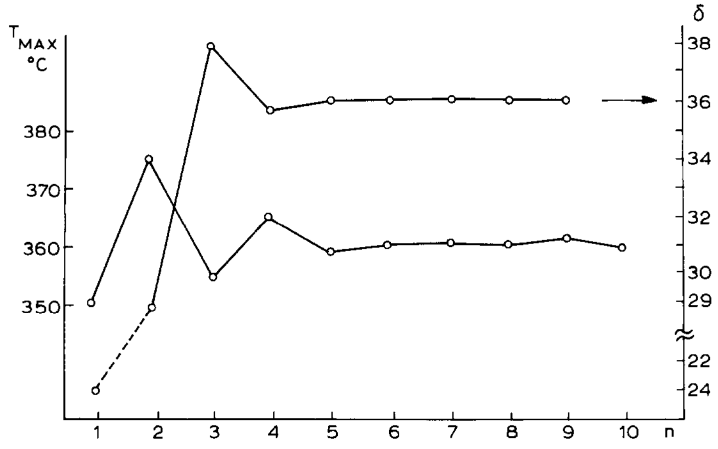

Fig. 10. Chemical shift of Cl′ atom and T_{max} obtained by MTA at a heating rate of 0.5 K min^{-1} vs. number of methylene groups in PAS samples.

CS. It should be noted that PAS-1 slightly deviates from the precise correlation between T_{max} and CS. This fact is probably related to the change in the character of carbon atom 1′ in the alkyl group (primary instead of secondary atom).

Hence, the observed odd–even effect of thermal stability is related to the change in the electron density of the macromolecule and confirms the above hypothesis.

As can be seen from Fig. 7, a decrease in the heating rate to 0.5 K min^{-1} in MTA leads to a considerable change in the character of the dependence of T_{max} on the length of the alkyl substituent. The authors suppose that, when heating is slow, this change in dependence is due to a longer time of existence of the polymers in the first range of thermal transformations, which leads to a more intensive development of chain processes. In this case, one may note the agreement between the thermal stability and the CS value for carbon atom 1′ of the alkyl substituent (Fig. 10). This fact suggests that, in contrast to the case of thermal degradation at a high heating rate (when the formation of a radical in the main chain is the limiting stage), in the case of thermal degradation of the polymer under conditions of slow heating, the process is limited by a reaction in the side chains with the formation of benzyl macroradicals of the PAS-117 type. The generated macroradicals start a chain of transformations leading finally to the depolymerization of the macromolecule.

These data confirm again the fact that, in the initial stages of the process at relatively low temperatures, crosslinked and other structures different from the initial structures can be formed and can also affect the subsequent process of thermal degradation of the sample.

In order to complete the discussion of experimental data, it is necessary to consider the curves of the dependence of T_{max} on the length of the substituent obtained by TGA and DSC. In contrast to MTA, these curves were obtained under atmospheric pressure. Although the heating rate was 6 K min^{-1}, these curves have a greater resemblance to the dependence obtained by MTA at a heating rate of 0.5 K min^{-1}. They exhibit a distinct alternation of T_{max} for the four first members of the series and closer values for all the following members, although for them too the odd–even effect is observed. In contrast to MTA, in which at a rate of 0.5 K min^{-1} the value of T_{max} for the six last polymers occupies an intermediate position between the maximum and minimum values, in the DTG and DSC experiments a cerain increase in T_{max} with respect to the first members of the series is observed. This effect may be explained by the influence of diffusion factors, which depend to a considerable extent on the pressure under which the reaction takes place and on the volume and the aggregate state of the sample. Under the conditions of high vacuum (MTA) and smaller sample feeds, low molecular weight compounds and free radicals are more intensively eliminated as compared with the conditions of TGA and DSC. In those cases when there is no intensive removal of products (TGA and DSC), the number of crosslinks in the first range of thermal transformations can increase. This increase, in turn, can lead to a certain increase in thermal stability.

In conclusion, it should be noted that, at present, charge alternation in the benzene ring of PAS depending on the length of the alkyl substituents cannot be explained satisfactorily, and further investigations are required.

CONCLUSIONS

1. In the investigation of chemical properties of polymers by MTA, TGA and DSC, an odd–even effect of chemical stability of PAS depending on the number of methylene groups in the alkyl substituent was detected.
2. It was shown that the dependence of thermal stability in the PAS series on the length of the alkyl radical agrees with the changes in the CS values on the carbon atoms of the benzene ring and the alkyl substituent, which shows that the odd–even effect is of electronic nature.
3. It was established that the character of the dependence of thermal stability on the PAS structure can change with the heating rate and the medium in which the polymer is heated.
4. The reason for these changes in dependence is the change in the processes of degradation, crosslinking, disproportionation, formation of macroradicals, etc., the intensity of which depends on the time and conditions of existence of the polymer in the low-temperature range (150–300 °C).

ACKNOWLEDGMENTS

The authors express their gratitude to L. Lajunen and P. Kokkonen (University of Oulu, Finland) for help in carrying out the experiments and for discussion of the results.

REFERENCES

1 D.N. Andreev, N.A. Solovskaya, V.A. Lukiashina, S.K. Zakharov and Yu.M. Boyarchuk, Plast. Massy, (3) (1987) 55.
2 Japanese Patent 61-9436, 1984.
3 W.W. Kaeding and G.G. Barile, Polym. Sci. Technol., 25 (1984) 223.
4 U.K.O. Schröder, Makromol. Chem., 188 (1987) 561.
5 U.K.O. Schröder, Makromol. Chem., 188 (1987) 2775.
6 D.N. Andreev, N.D. Solovskaya, S.K. Zakharov and V.A. Lukiashina, Plast. Massy, (2) (1984) 58.
7 L.A. Shibaev, Yu.N. Sazanov, N.G. Stepanov, T.M. Bulina and T.I. Zhukova, Vysokomol. Soedin., Ser. A, 24 (1982) 2543.
8 G.G. Cameron and G.P. Kerr, Eur. Polym. J., 6 (1970) 423.
9 P.C. Lauterbur, J. Am. Chem. Soc., 83 (1961) 1838.
10 E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, Verlag Chemie, Weinheim, 1978, p. 344.
11 Ch.K. Ober, J.-J. Jin and R.W. Leus, Adv. Polym. Sci., 59 (1984) 103.
12 J. March, Advanced Organic Chemistry. Reactions, Mechanisms and Structure, Wiley-Interscience, New York, 3rd edn., 1985.
13 V.V. Zuev, Thesis, Institute of Macromolecular compounds of the Academy of Sciences of the USSR, Leningrad, 1988.
14 V.V. Zuev, A.Yu. Elkin, A.V. Gribanov and S.S. Skorokhodov, Vysokomol. Soedin., Ser. A, 29 (1987) 780.
15 V.V. Zuev, I.G. Denisov and S.S. Skorokhodov, Vysokomol. Soedin., Ser. A, 31 (1989) 1056.