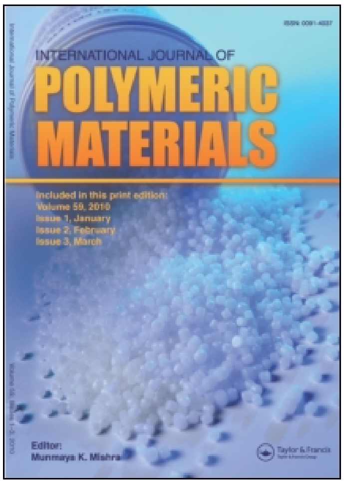

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Sazanov, Yu. N. , Shibaev, L. A. , Stepanov, N. G. and Sokolovskaya, N. A.(1990) 'Relationships of Thermal Degradation of Homologous Series of Polyalkylstyrenes and Polyalkylacrylates', International Journal of Polymeric Materials, 14: 1, 85 — 90

To link to this Article: DOI: 10.1080/00914039008041074

URL: http://dx.doi.org/10.1080/00914039008041074

Intern. J. Polymeric Mater., 1990, Vol. 14, pp. 85–90
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Printed in the United Kingdom

Relationships of Thermal Degradation of Homologous Series of Polyalkylstyrenes and Polyalkylacrylates

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The thermal stability and degradation products of the polyalkylstyrenes and polyalkylacrylates homologous series have been investigated by mass-spectrometric thermal analysis. It was shown that crosslinking process is thermodynamically favorable in the initial stage of the thermal degradation. The dependence of thermal degradation mechanism and kinetic parameters on heating rate and alkyl radical length has been determined.

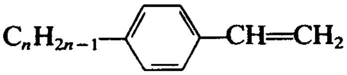
KEYWORDS: Polyalkylstyrenes, polyalkylacrylates, thermal degradation, homologous series

In most papers studying the thermal degradation of polystyrenes and polyacrylates, individual representatives of these polymer classes have been investigated by different methods under different conditions,[1] thus making it impossible to compare the results.

The present paper deals with the investigation of thermal stability of homologous series of polyalkylstyrenes and polyalkylacrylates under identical conditions. The effect of the heating rate of the samples under vacuum on the thermal characteristics and the degradation mechanism of these polymers was also determined.

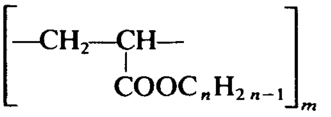
EXPERIMENTAL PART

The polymerization of 4-n alkylstyrenes with the formula



where $n = 0$–6 was carried out in bulk under helium in the presence of 0.2% of benzoyl peroxide at 70°C for 20–40 h. The intrinsic viscosity of polymers in toluene varied from 0.51 to 0.91 dl/g for various samples and the molecular weight was $5 \cdot 10^5$–10^6.[2]

Poly-*n*-alkylacrylates with the formula



$$\left[-CH_2-\underset{\displaystyle COOC_nH_{2n-1}}{\underset{|}{CH}}- \right]_m$$

where $n = 1, 2, 4, 5, 6, 7, 8, 10, 12$ were obtained by the photopolymerization of the corresponding monomers in a chloroform solution in the presence of benzoyl peroxide at room temperature.

The thermal degradation of polymers was investigated by mass-spectrometric thermal analysis with an MX 1320 mass spectrometer at a heating rate of 0.5, 2 and 6 K/min.

The current temperature of the samples was determined with an inner thermocouple on which the sample with a mass of about 0.1 mg was fixed with aluminium foil. The mass spectra of the products were taken at the energy of ionizing electrons of 70 eV and were recorded with a light beam oscillograph with the periodicity of 1–3 min.

DISCUSSION OF RESULTS

The degradation of polystyrene has been investigated in detail in the literature, whereas the thermal behavior of poly (*p*-alkylstyrenes) has drawn much less attention. Such representatives of this class as poly (*p*-ethylstyrene), poly (*p*-isopropylstyrene), poly(*p*-tert-butylstyrene) and poly (*p*-methylstyrene) have been investigated.[3–6] In the study of the degradation mechanism, it has been established that under the conditions of isothermal heating some of these polymers form a three-dimensional network, whereas polystyrene does not form it. On the basis of these results, it might be expected that the thermal stability of individual representatives of this series differs greatly.

Our investigation of the thermal degradation of poly (*p*-alkylstyrenes) by mass spectrometric analysis under the conditions of non-isothermal heating at a constant rate of 2 K/min showed (Table I) that the lowest thermal stability determined from both the initial part of the process and the temperature of the maximum degradation rate (T_{max}) is observed for poly (*p*-methylstyrene). The temperature at which the reaction rate was 10% of the maximum rate ($T_{10\%}$) was chosen as the criterion for the start of thermal degradation. Under the above conditions, the maximum thermal stability was observed for poly (*p*-ethylstyrene).

It is noteworthy that the peaks of maximum intensity in the mass spectra of poly (*p*-alkylstyrenes) are the peak with the mass 117 and that of the molecular ion. The peak with the mass 117 corresponds to the resonance-stabilized structure which can be that of the fragmentary ion formed during the ionization of the

TABLE I

Thermal characteristics of *p*-substituted polyalkylstyrenes

Substituent	T_{max}, °C	$T_{10\%}$, °C
—	383	340
methyl	375	333
ethyl	395	343
propyl	385	342
butyl	391	342
amyl	393	—
hexyl	382	343

T_{max} is the temperature of the maximum reaction rate. $T_{10\%}$ is the temperature at which the reaction rate is 10% of the maximum rate.

monomer in the ion source of the instrument. These facts indicate that the main products of thermal degradation of poly (*p*-alkylstyrenes) are the corresponding monomers and hence degradation proceeds by the depolymerization mechanism.

In order to determine the effect of crosslinking on the thermal characteristics of polystyrenes, samples containing bifunctional crosslinking agents, e.g., dimethacrylic ester of ethylene glycol (DMEG) were synthesized. In these samples the thermal stability of crosslinks is not inferior to that of the main polymer. It was found that the thermal characteristics of poly (*p*-ethylstyrene) synthesized with the addition of 15 mole% of DMEG are not improved as compared to those of the uncrosslinked polymer. Hence, it may be said that under the conditions of dynamic heating of samples, crosslinking does not affect the thermal characteristics of polymers.

Those facts also provide the explanation of the most inferior thermal characteristics of poly (*p*-methylstyrene) in the homologous series. The high trend of this polymer towards crosslinking under the conditions of isothermal heating[3] evidently indicates that the free radical is formed in the macromolecule relatively easily. This may be associated with the possibility of delocalizaiton of the unpaired electron as a result of the hyperconjugation of the methyl substituent with the aromatic ring. The resulting radial can either lead to crosslinking or initiate depolymerization. Since under the conditions of non-isothermal heating crosslinking has no thermally stabilizing effect on the polymer, the increasing free radical concentration is manifested in the acceleration of polymer degradation as a result of the increasing rate of initiation of the chain depolymerization process. Hence, the thermal characteristics of poly (*p*-methylstyrene) became inferior.

On passing to another homologous series of vinyl polymers, poly-*n*-alkylacrylates, it should be noted that their thermal degradation does not proceed by the depolymerization mechanism, and the main degradation products are carbon dioxide and the corresponding alcohol.[1,7] Figure 1 shows the yield curves of these products during the thermal degradation of polyethylacrylate. It is clear that the temperature of the peak maximum of carbon dioxide yield is slightly higher than that of the alcohol. This difference is maintained irrespective of the nature of the alkyl substituent and the heating rate (Table II), and the series of

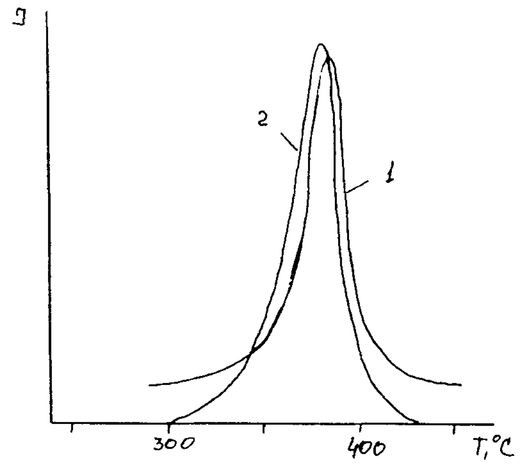


FIGURE 1 Yield curves of (1) carbon dioxide (m/e 44) and (2) ethyl alcohol in the course of thermal degradation of polyethylacrylate at a rate of 6 K/min.

thermal stability determined from the yield of carbon dioxide and the alcohol correspond to each other.

The consideration of thermal characteristics of the homologous series of polyacrylates also confirms the fact that these characteristics depend on the conditions under which the polymers are tested or on service conditions. Thus, under identical conditions of non-isothermal heating in vacuum, the temperatures of the start and the maximum degradation rates of a homologous series of polymers with similar chemical compositions depend on the heating rate, although the range of rate changes is not very wide: from 0.5 to 6 K/min.

At a heating rate of 2°/min, polymethylacrylate exhibits the lowest thermal stability. It is followed by polyethylacrylate, whereas other polymers beginning

TABLE II

Thermal characteristics of polyalkylacrylates as a function of the heating rate of the polymer under vacuum determined from the yield curves of CO_2 and the corresponding alcohol

	T_{max}, °C, at a heating rate of:						$T_{10\%}$, °C, at a heating rate of					
	0.5 K/min		2 K/min		6 K/min		0.5 K/min		2 K/min		6 K/min	
Substituent	CO_2	alcohol	CO_2	alcohol	CO_2	alcohol	CO_2	alcohol	CO_2	alcohol	CO_2	alcohol
methyl	331	326	331	324	356	340	286	270	296	290	304	303
ethyl	311	308	336	331	385	383	276	272	305	305	344	338
butyl	329	327	360	359	367	361	292	287	317	303	320	305
amyl	339	338	362	360	378	377	—	—	320	—	340	330
hexyl	343	330	355	355	380	380	—	283	320	305	341	333
heptyl	335	332	356	352	371	365	302	298	320	305	332	317
octyl	336	336	364	362	376	370	300	287	322	305	330	318
decyl	338	339	359	356	378	378	307	290	320	304	328	325
dodecyl	341	338	360	354	378	372	308	295	325	301	336	325

from polybutylacrylate exhibit higher and approximately the same thermal stability. At a heating rate of 0.5 K/min, polyethylacrylate is the least stable, whereas at a rate of 6 K/min it is the most stable polymer.

This can be more clearly seen in the plot of the dependence of $\ln v/T_{\max}^2$ on $1/T_{\max}$ (Figure 2). The tangent of the slope angle of this plot is $-E_{\mathrm{act}}/R$ irrespective of the reaction order. The plot shows distinctly two groups of polymers differing in thermal behavior.

The first group includes polymethyl- and ethylacrylates. It can be seen that in the chosen system of coordinates the degradation of these polymers is not described by a straight line. The dependence of the activation energy on the heating rate may be explained by the change in the degradation mechanism. This is particularly expressed for polymethylacrylate and is evidently due to the peculiar behavior of the methoxy group.

The fact that the temperatures of the peak maxima of the yield of carbon dioxide and methanol at a heating rate of 0.5 and 2 K/min virtually coincide (Table II) suggests that by analogy with poly (*p*-methylstyrene) the change in the reaction mechanism may be due to crosslinking. At low heating rates, the rate of crosslinking is comparable to that of the degradation of the main chain and during

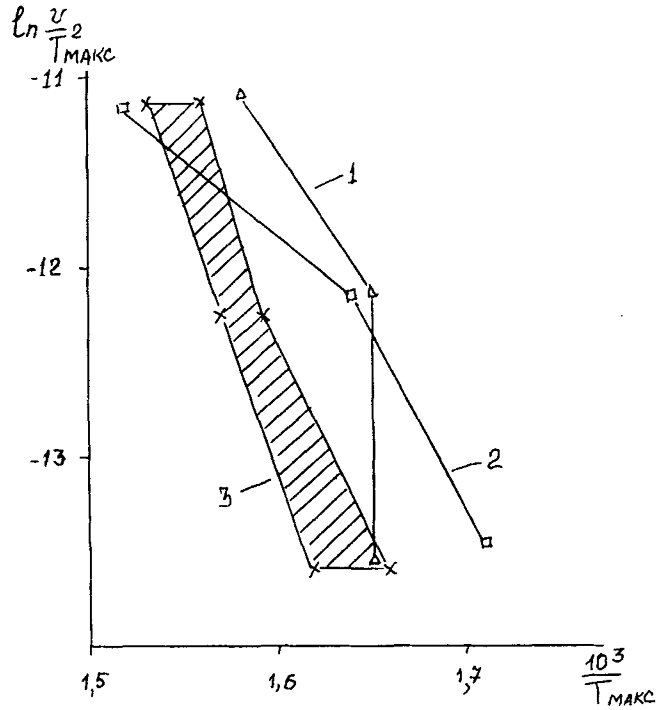


FIGURE 2 Dependence of $\ln v/T_{\max}^2$ on $10^3/T_{\max}$ for the yield of carbon dioxide. v—heating rate, K/min; $T_{\max}$—the temperature of the peak maximum for the yield of carbon dioxide, °K. (1) for polymethylacrylate, (2) for polyethylacrylate, (3) the range of values for polymers from polybutylacrylate to polydodecylacrylate.

slow heating, the crosslinked structure can be formed, which ensures higher thermal stability of the polymer in the initial degradation stages.

In the case of a higher heating rate, crosslinks cannot yet be formed because the temperature range in which crosslinking is possible continues for a very short time.

In other words, the crosslinking process in the initial stage of thermal degradation of poly (methyl methacrylate) is thermodynamically favorable but at high heating rates crosslinking cannot occur for kinetic reasons.

This treatment can evidently serve as an alternative explanation of low thermal stability of poly (*p*-methylstyrene) is the homologous series of polyalkylstyrenes considered above.

The degradation of polyethylacrylate is characterized by a lower averaged value of activation energy than that of the other representatives of the polyalkylacrylate series (~150 kJ/mole). This low value explains the fact that the polymer exhibits the lowest thermal characteristics at low heating rates and the highest characteristics at high rates.

The second group includes all the other investigated polymers from butylacrylate to dodecylacrylate. The degradation of all these polymers proceeds virtually in the same manner irrespective of the length of the alkyl substituent, and the process may be adequately described by a straight line in the system of coordinates used. In this case the activation energy is about 250 KJ/mole.

Hence, several conclusions may be drawn from the results of these investigations:

- In the series of vinyl polymers under the conditions of dynamic heating in vacuum, polyalkylstyrenes are found to be more thermally stable than polyalkylacrylates.
- both in the polyalkylstyrene series and in that of polyacrylates the increase in the length of the alkyl substituent does not decrease the thermal characteristics of the polymers.
- the peculiar role of the methoxy group was shown taking polymethylacrylate as an example. It is expressed in the dependence of the activation energy of thermal degradation on the heating rate.
- in the polyalkylacrylate series, polyethylacrylate should be singled out as exhibiting the lowest activation energy of thermal degradation process.

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