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STUDY OF THE THERMAL BEHAVIOUR OF COPOLYMERS OF STYRENE WITH MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM ACRYLATES

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The processes of thermal destruction of copolymers of styrene with magnesium, calcium, strontium and barium acrylates have been investigated by TG and the temperature characteristics have been determined. Though the thermal stability of the metal acrylates exceeds markedly that of polystyrene, the introduction of low concentrations of the salts caused an observable deterioration of the thermal resistance of the copolymers. This was in agreement with the calculated values of the kinetic parameters of decomposition for the samples studied.

Investigations of the thermal stability of polymers by thermogravimetric analysis are widely used for rapid assessment of their relative chemical resistance at high temperatures. This method offers a means to determine quickly the contributions of different chemical structures to the thermal stability of the polymer on the basis of several comparative criteria obtained under the same conditions. The calculation of kinetic parameters of thermal degradation furnishes additional data on its characteristics and is often helpful in establishing the mechanism of decomposition. Although the values of kinetic parameters are useful in the comparison of the processes of thermal degradation occurring under identical conditions, these values should be treated as only formal criteria.

Metal-containing polymers are often thermally stable and chemically resistant [1]. Ionomers examined primarily have been obtained in two stages. A component containing groups capable of ionization has been introduced into a non-ionic skeleton and the groups have been subjected to total or partial ionization. An alternative method, becoming more popular in recent

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years, is a direct copolymerization of a non-ionogenic monomer with an ion-containing one.

We have previously studied the thermal decomposition of zinc(II), cobalt(II), nickel(II) and copper(II) acrylates and their polymers [2], as well as that of several alkali and alkaline earth metal acrylates and methacrylates [3]. The thermal behaviour of some transition metal acrylate-styrene copolymers [4] and copolymers of styrene with lithium, sodium and potassium acrylates and methacrylates [5] has also been investigated. In extension of these studies, the present paper is concerned with the thermal stabilities of styrene copolymers with magnesium, calcium, strontium and barium acrylates obtained in a process of a direct copolymerization.

Experimental

Materials

Styrene, acrylic acid, dimethyl sulfoxide and methanol, all commercial grade, were purified according to standard procedures. 2.2'-Azobisisobutyronitrile (AIBN) (Koch-Light Laboratories, England) was recrystallized twice from methanol (m. p. ≈ 103°).

Preparation of metal acrylates

The monomeric salts were prepared by neutralization of a methanolic solution of the appropriate hydroxide with acrylic acid at ca. 8°. The reaction mixture was poured into excess acetone. The precipitated salts were filtered off, washed with acetone to remove acid and vacuum dried at room temperature to constant weight. The composition of monomers was characterized by determination of metal and double bond contents, as well as TG investigations.

Preparation of copolymers

Copolymerization of styrene with alkaline earth metal acrylates (A_2Mt) was performed at 70°. The general copolymerization procedure has been described [6]. The reaction mixtures were composed of dimethyl sulfoxide (200 cm^3), AIBN (0.5 g) and monomers (100 g).
Contents of acrylate salts in the mixtures varied in the range: A_2Mg (1-5), A_2Ca (1-10), A_2Sr (1-15), A_2Ba (0.5-5) weight-%. Under such conditions homogeneous copolymerization occurred resulting in copolymers soluble in

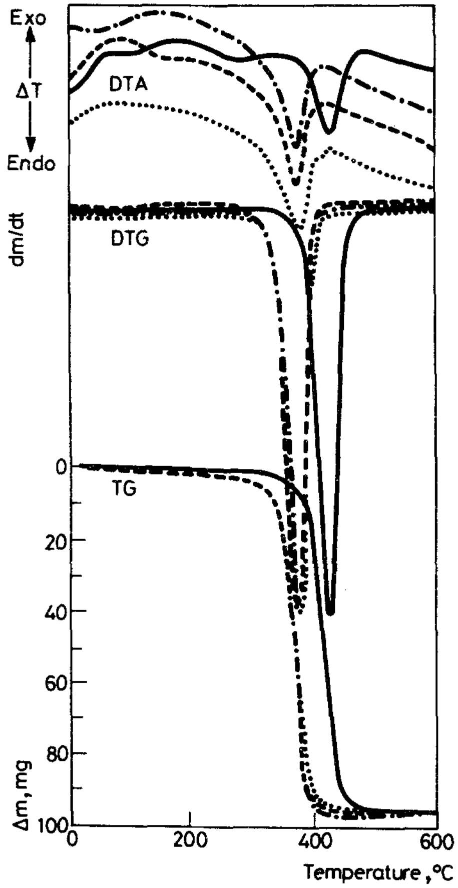

Fig. 1 TG, DTG and DTA curves of styrene copolymers containing Mg acrylate (0.355 mole %)(······), Ca acrylate (0.375 mole %)(–·–), Ba acrylate (0.366 mole %) (– – –) and polystyrene (——)

solvents for polystyrene. Reactions were stopped by pouring the reaction systems into a large excess of cold methanol. The precipitated copolymers were filtered off, washed with methanol, dissolved in chloroform and again precipitated with methanol. Purified copolymers were vacuum dried at 50° to constant weight. Reaction times were different for individual systems and chosen in such a way that the yields of copolymerization were kept within the limit of 3 to 6 wt.-%. The compositions of copolymers were determined from the metal contents.

Thermal analysis

TG, DTG and DTA curves were recorded simultaneously using a Paulik - Paulik - Erdey derivatograph (Type OD-102, MOM, Budapest). 100 mg of powdered sample was heated in a Pt crucible at temperatures up to 600° in a nitrogen atmosphere (20 1/hr) at a constant heating rate of 3 deg/min. The sensitivity of the instrument was 1/3 for DTA and DTG.

The reaction orders (n) and activation energies of decomposition (E_a) were determined by the Horowitz-Metzger method [7]. The preexponential factor (Z) and the entropy of activation (ΔS) were calculated as reported previously [4, 5].

Results and discussion

Thermal behaviour of copolymers

Figure 1 shows the thermal curves of the copolymers containing about 0.4 mole % of Mg, Ca, and Ba acrylates, as examples of the thermal decomposition of copolymers containing various kinds of metal acrylates.

The thermal degradation process takes place in one stage, as indicated by the mass loss, accompanied by an endothermic peak in the DTG curve in the range 310-420°. TG and DTG curves of all investigated ionomers resemble those of polystyrene. This is undoubtedly due to a high styrene content in copolymers and the dominant role of decomposition reactions of these segments of macromolecules.

More detailed data concerning the thermal degradation of all copolymers under study are given in Table 1.

From Table 1 it is seen that in general the maximum rates of decomposition correspond to the temperatures where about 60 % weight loss is observed.

The changes of IDT, DT at different weight losses and T_s for the copolymers in relation to polystyrene indicate a similar pattern of thermal resistance. Marked decreases of thermal stability of copolymers are observed within the investigated ranges of copolymer compositions but no clear trends can be seen when the salt content in the copolymer increases. In all cases the thermal resistance of copolymers is lower than that of polystyrene as a reference. Decomposition temperatures of copolymers are on the whole by about 30-50° lower than those of PS. It is noteworthy that such a change of thermal stability is caused by a very low content of alkaline earth metal acrylates whose thermal stabilities ($T_S \approx 500^{\circ}$) exceed markedly that of polystyrene [3].

Table 1 Thermal characteristics of styrene copolymers containing magnesium acrylate (No. 2 - 6), calcium acrylate (No. 7 - 12) , strontium acrylate (No. 13 - 18) and barium acrylate (No. 19 - 23). For comparison, corresponding data for polystyrence, obtained under the same conditions, are also given (No.1)

	Metal content	Metal acrylate	IDT*, DT** at different weight losses						T_s^{***}
No.	in copolymer,	content in copolymer,		10 %	20 %	40 %	60 %	80 %	
	wt %	mole %	°C						
1	–	–	317	383	401	412	424	431	422
2	0.056	0.239	300	356	366	377	386	394	390
3	0.083	0.355	290	343	354	364	371	380	375
4	0.146	0.606	270	333	347	357	367	377	374
5	0.197	0.848	300	360	370	379	388	397	390
6	0.411	1.779	280	348	361	371	380	391	387
7	0.067	0.175	250	330	348	366	376	382	375
8	0.144	0.375	285	343	355	370	375	380	374
9	0.258	0.675	295	348	360	370	380	392	383
10	0.381	0.994	295	340	350	360	370	377	370
11	0.640	1.677	300	347	360	371	383	390	383
12	0.746	1.966	275	330	350	367	378	392	379
13	0.19	0.226	295	342	352	362	372	380	373
14	0.37	0.440	295	348	360	366	380	391	383
15	0.66	0.798	280	344	355	368	377	381	380
16	1.34	1.623	280	346	359	369	379	388	380
17	1.62	1.973	280	341	356	367	376	380	378
18	3.01	3.738	270	326	351	366	377	391	380
19	0.14	0.106	290	356	368	380	399	400	390
20	0.25	0.190	300	349	359	367	375	386	380
21	0.48	0.366	280	337	349	361	372	378	373
22	0.89	0.683	270	339	353	367	376	386	380
23	1.30	1.002	290	328	344	359	371	380	372

IDT* = initial decomposition temperature, DT** = decomposition temperature read off the TG curve at a given weight loss, T_s*** = temperature corresponding to the maximum rate of decomposition, read off the DTG peak.

It has been reported in the literature that polystyrene decomposes mainly by depropagation [8] and a "zipper"-type mechanism is involved. It seems that the presence of alkaline earth metal acrylate-mers in copolymer molecules facilitates the opening of that "zipper" and thus degradation is promoted. This initiation stage of decomposition would be expected to be almost independent of the metal acrylate concentration in the copolymer.

Table 2 Kinetic parameters of decomposition of styrene copolymers containing magnesium acrylate (No. 2 - 6), calcium acrylate (No. 7 - 12), strontium acrylate (No. 13 - 18) and barium acrylate (No. 19 - 23). For comparison, corresponding data for polystyrene, obtained under the same conditions, are also given (No.1). Order of reaction, $n = 1$, is the same in all cases

No.	Metal content in copolymer, wt %	Metal acrylate content, mole %	E_a, kJ/mole	Z, s^{-1}	ΔS J/mole K
1	–	–	248	1.4×10^{16}	57.1
2	0.056	0.239	237	1.5×10^{16}	58.1
3	0.083	0.355	229	9.5×10^{15}	54.5
4	0.146	0.606	206	1.3×10^{14}	18.7
5	0.197	0.848	227	1.4×10^{14}	19.9
6	0.411	1.779	198	1.3×10^{13}	-0.5
7	0.067	0.175	194	1.2×10^{13}	-0.9
8	0.144	0.375	206	1.3×10^{14}	18.7
9	o.258	0.675	223	1.7×10^{15}	40.5
10	0.381	0.994	233	2.9×10^{16}	63.8
11	0.640	1.677	208	1.1×10^{14}	17.1
12	0.746	1.966	174	2.2×10^{11}	-34.4
13	0.19	0.226	224	4.2×10^{15}	47.8
14	0.37	0.440	241	5.3×10^{16}	68.6
15	0.66	0.798	214	4.0×10^{14}	28.1
16	1.34	1.623	222	1.8×10^{15}	40.6
17	1.62	1.973	207	1.2×10^{14}	18.1
18	3.01	3.738	170	9.6×10^{10}	-2.9
19	0.14	0.106	243	4.7×10^{16}	67.6
20	0.25	0.190	237	3.1×10^{16}	64.2
21	0.48	0.366	220	2.0×10^{15}	41.4
22	0.89	0.683	200	2.8×10^{13}	6.1
23	1.30	1.002	189	5.6×10^{12}	-7.3

The results obtained are not in accordance with our previous findings concerning the thermal behaviour of similar styrene - based systems. The thermal stabilities of copolymers of styrene with lithium and potassium acrylates [5] were comparable with that of polystyrene and practically independent of the amount of alkali metal acrylates introduced into copolymers. However, even a very little amount of sodium salt in copolymers [5] led to a noticeable increase of their thermal resistance. The thermal stability of zinc - containing copolymers [4] increased clearly with increasing zinc acrylate content up to 22.6 mole %. Small amounts of A_2Co, A_2Ni and A_2Cu improved the thermal resistance of copolymers [4], which then gradually dropped at higher concentrations of the salts. When the nickel acrylate content is about 10 mole %, the decomposition temperatures of the copolymers are about 25^0 lower than those of polystyrene. The experimentally found thermal stability of styrene copolymers containing different metal acrylates [4, 5] corresponds to those of the respective poly(metal acrylates) [2, 3]. However, the thermal behaviour of the macromolecules cannot be correlated with any specific property of the metals. Similarly, there is no relation of the thermal resistance of the investigated copolymers with the properties of alkaline earth metals. Thus, it may be supposed that in the case of these copolymers a different mechanism of initiation of degradation is involved. This indicates a complex role of metal ions in affecting the thermal stability of polymers. As recognized earlier [9], metal ions may both increase the thermal resistance of the compounds, as well as facilitate their decomposition since many factors are involved.

Kinetic parameters of copolymer decomposition

The calculated kinetic parameters: reaction order (n), the activation energy of the main stage of decomposition (E_a), the preexponential factor (Z) and the entropy of activation (ΔS) are given in Table 2.

The order of reaction for the main decomposition step of all investigated copolymers was equal to one, similarly as for the comparative PS as well as for alkali acrylates containing copolymers [5].

The determined activation energies of the main stage of decomposition for copolymers are lower than that of polystyrene. Thus, the same trend as resulting from consideration of thermal stability is maintained. The tendency for decreasing E_a values with increasing salt content in the copolymers can be noticed in some cases. However, the values of activation energies of decomposition should not be considered separately, as the values of the activation entropy (ΔS) are also important. The latter values are in general moderate; this is in agreement with the assumption that in a unimolecular reaction the activated complex may be expected to resemble the initial state. For some copolymers negative values of ΔS were obtained and this indicates that the activated complexes have more ordered structures than those of the reactants. This decrease in ΔS, though unfavourable for an enhanced rate of decomposition, is compensated for by smaller E_a values. The mutual correlation between kinetic parameters is often observed and known in the literature as the "kinetic compensation effect" [10-13].

The calculated values of the kinetic parameters E_a, ΔS and Z are comparable with those obtained by us for the thermal decomposition of styrene copolymers with alkali metal acrylates [5], as well as with some transition metal acrylates [4].

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Zusammenfassung — Mittels TG wurde der thermische Abbauvorgang von Kopolymeren aus Styrol und Magnesium-, Calcium-, Strontium- und Bariumacrylaten untersucht und eine Temperaturcharakteristik erstellt. Obwohl die thermische Stabilität der Metallacrylate die von Polystyrol eindeutig übertrifft, führt die Einführung dieser Salze in geringer Konzentration zu einer merklichen Verschlechterung der Hitzebeständigkeit der Kopolymere. Diese Feststellung stimmt mit den für die Zersetzung der untersuchten Proben berechneten kinetischen Parametern überein.