

STUDY OF THE THERMAL BEHAVIOUR OF SOME TRANSITION METAL ACRYLATE–STYRENE COPOLYMERS*

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The processes of thermal destruction of copolymers of styrene with zinc, cobalt, nickel and copper acrylates have been studied by TG and the temperature characteristics have been determined. While the thermal stability of zinc-containing copolymers increases at higher metal contents, that of other metal-containing copolymers decreases and, depending on the metal, changes in the sequence $\text{Co} > \text{Ni} > \text{Cu}$.

The kinetic parameters n , E_a , Z and ΔS have been determined by the Horowitz–Metzger method and discussed. The resulting E_a sequence is in agreement with the observed sequence of thermal stability of the copolymers. The entropy factor suggests thermodynamic hindrance in the decomposition of copolymers of low thermal stability and a preference for the decomposition of copolymers of high thermal stability.

The thermal degradation of polymers has often been studied, but investigations on the thermal behaviour of copolymers prepared from metal-containing monomers are scarce. The dependences of the yield and the mechanism of degradation on the content of some alkali metal methacrylates in copolymers with methyl methacrylate have been investigated [1]. A thermogravimetric study [2] of styrene–acrylic acid copolymers and their sodium salts containing up to about 15 mole% of polar mers revealed the higher thermal stabilities of the salt derivatives than those of the parent copolymers and polystyrene.

We have previously studied [3] the thermal decompositions of zinc(II), cobalt(II), nickel(II) and copper(II) acrylates and their polymers. In the present work we have made an attempt to characterize the thermal stabilities and kinetics of decomposition of copolymers of these metal acrylates with styrene.

Experimental

The preparation of the copolymers and the conditions of thermal analysis have been described previously [3, 4].

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Determination of kinetic parameters

The reaction orders (n) and activation energies of decomposition (E_a) were determined by the Horowitz–Metzger method [5].

The preexponential factor (Z) and the entropy of activation (ΔS) were calculated from the equations [6]

$$\frac{E_a}{RT_s^2} = \frac{Z}{\varphi} n C_s^{n-1} e^{-\frac{E_a}{RT_s}} \quad (1)$$

and

$$\Delta S = R \ln \frac{Zh}{kT_s} \quad (2)$$

where k is the Boltzmann constant, h is Planck's constant, φ is the heating rate, C_s is a parameter related with the sample weight [5] and T_s is the temperature corresponding to the maximum rate of decomposition, read off the DTG peak.

Results and discussion*Thermal behaviour of copolymers*

Figure 1 shows the thermal curves of the copolymers containing about 7 mole% of Zn, Co and Ni acrylates, as examples of the thermal decomposition of copolymers containing various kinds of metal acrylates.

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 60% weight losses are observed.

The changes of IDT, DT at different weight losses and T_s for the copolymers in relation to polystyrene indicate various patterns of thermal resistance. The thermo-stability of zinc-containing copolymers increases with increasing metal content, while those of other metal-containing copolymers decrease with intensities depending on the nature of the metal. The observed thermal stability sequence for the copolymers, $A_2Zn-St > A_2Co-St > A_2Ni-St > A_2Cu-St$ (A_2M = metal acrylate, St = styrene), is in good agreement with the observed thermal stability sequence for the corresponding metal acrylates and polyacrylates [3].

Zinc-containing compounds have often been found to possess high thermal stability [3, 7–9]. This may be due [8] to the pseudo-inert gas structure of zinc(II) and its existence in only one oxidation state. The higher thermal stability of zinc acrylate and polyacrylate [3] relative to polystyrene indicates the thermal reinforcement to a copolymer. The lowering of the thermal stabilities of styrene copolymers with cobalt, nickel and copper acrylates may be explained by the catalytic action of these transition metal ions, facilitating thermal decomposition. Polyvalent cations capable of

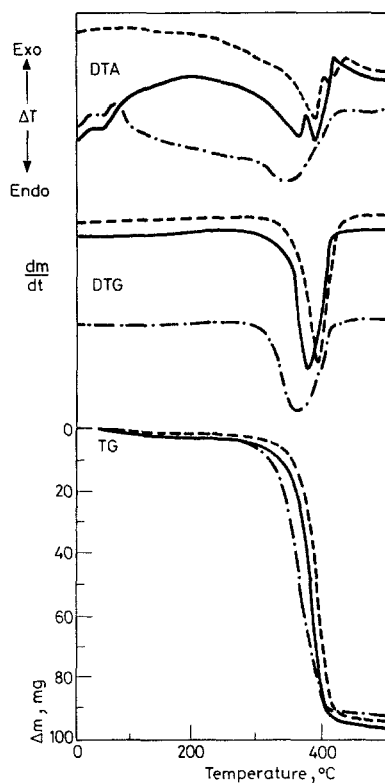


Fig. 1 TG, DTG and DTA curves of styrene copolymers containing Zn acrylate (6.98 mole%) (---), Co acrylate (7.06 mole%) (—) and Ni acrylate (6.18 mole%) (-.-.-)

playing the role of oxygen-transfer agents may decrease the thermostability of the compounds. It was found [10] that, due to its ability to exist in variable valence states, the cobalt ion promotes electron transfer in the propagation step of polystyrene degradation, increasing the rate of propagation and consequently the overall rate. It is also known [11] that the reductions of cobalt and nickel oxides are autocatalytic in character, while no catalytic action of the reduced metal was observed in the case of zinc oxide. The poor thermal stability of copper-containing compounds has often been reported [3, 12–15].

It has been established that PS decomposes mainly by depropagation, and the controlling factor in the mechanism of the degradation is the nature of the side-group attached to the carbon atom at which chain scission occurs [16]. Introduction of the electron-withdrawing side-substituent may be responsible for the lower initial decomposition temperature. Investigation of the metal acrylates has shown [4, 17] the dependence of their reactivities in polymerization and copolymerization on the nature of the metal. The different reactivities of these monomers were correlated [4] to the

Table 1 Thermal characteristics of styrene copolymers containing zinc acrylate (nos 2–8), cobalt acrylate (nos 9–15), nickel acrylate (nos 16–22) and copper acrylate (nos 23–29). For comparison, corresponding data for polystyrene, obtained under the same conditions, are also given (no. 1)

No.	Metal content in copolymer in wt%	Metal acrylate content in copolymer in mole%	IDT*, °C	DT** at different weight losses					T_g , °C
				10%	20%	40%	60%	80%	
1	—	—	285	344	356	367	375	383	375
2	2.16	3.56	270	350	370	386	395	406	395
3	3.35	5.63	275	355	372	386	397	408	396
4	4.10	6.98	287	355	370	386	398	409	397
5	5.25	9.11	285	347	364	380	390	405	397
6	8.30	14.69	315	375	387	404	415	433	413
7	10.30	19.58	325	383	398	412	421	445	418
8	11.60	22.60	332	385	400	414	423	460	420
9	0.515	0.92	312	360	374	387	399	408	400
10	1.23	2.22	304	352	369	384	396	405	398
11	1.74	3.16	300	342	364	380	390	402	396
12	2.50	4.60	293	340	362	377	388	399	388
13	2.97	5.51	288	335	360	377	387	399	389
14	3.75	7.06	284	338	364	379	388	400	384
15	4.20	7.97	280	327	353	375	386	398	381
16	0.60	1.07	305	360	374	387	396	407	395
17	1.76	3.21	280	332	347	364	377	390	377
18	2.49	4.60	265	313	335	354	368	384	365
19	3.30	6.18	260	307	327	344	358	376	355
20	4.02	7.63	267	315	335	352	368	388	360
21	4.99	9.63	265	313	333	349	364	385	350
22	5.50	10.72	263	308	329	349	364	384	350
23	0.078	0.128	278	348	362	378	389	402	390
24	0.105	0.172	277	347	360	375	387	399	385
25	0.23	0.38	278	347	361	378	390	404	390
26	0.33	0.54	275	335	353	370	385	400	385
27	0.53	0.88	270	330	347	365	379	395	380
28	0.81	1.34	267	329	347	365	380	396	380
29	1.18	1.97	260	320	338	360	373	390	375

* IDT = initial decomposition temperature, ** DT = decomposition temperature read off the TG curve at a given weight loss.

metal electronegativities changing the charge distribution on the vinyl groups. Similarly, side metal acrylate groups bonded to the carbon atom of the polymer chain may influence the ease of its thermal scission. For the electronegativity [18] E of the metals, that governs the electron-withdrawing power, $E_{Cu} = 1.9 > E_{Ni} = E_{Co} = 1.8 >$

Table 2 Kinetic parameters of decomposition of styrene copolymers containing zinc acrylate (nos 2–8), cobalt acrylate (nos 9–15), nickel acrylate (nos 16–22) and copper acrylate (nos 23–29). For comparison, corresponding data for polystyrene, obtained under the same conditions, are also given (no. 1)

No.	Metal content in copolymer in wt%	Metal acrylate content in mole%	n	E_a , kJ/mole	Z , s ⁻¹	ΔS , J/mole °K
1	—	—	1	263	5.0×10^{13}	106.7
2	2.16	3.56	1	208	4.3×10^{13}	9.5
3	3.35	5.63	1	209	4.9×10^{13}	10.5
4	4.10	6.98	1	206	2.7×10^{13}	5.4
5	5.25	9.11	1	212	8.1×10^{13}	14.6
6	8.30	14.69	1	259	1.5×10^{17}	76.8
7	10.30	19.58	1	287	1.5×10^{19}	115.3
8	11.60	22.60	1	290	2.2×10^{19}	118.4
9	0.515	0.92	1	217	1.7×10^{14}	20.7
10	1.23	2.22	1	212	7.6×10^{13}	14.1
11	1.74	3.16	1	201	1.1×10^{13}	-1.7
12	2.50	4.60	1	199	1.2×10^{13}	-0.9
13	2.97	5.51	1	197	8.0×10^{12}	-4.5
14	3.75	7.06	2	306	7.7×10^{21}	167.5
15	4.20	7.97	2	301	3.9×10^{21}	161.9
16	0.60	1.07	1	222	5.8×10^{14}	31.0
17	1.76	3.21	1	178	4.3×10^{11}	-28.6
18	2.49	4.60	3/2	171	2.1×10^{11}	-34.3
19	3.30	6.18	3/2	165	1.1×10^{11}	-39.5
20	4.02	7.63	2	192	1.7×10^{13}	2.1
21	4.99	9.63	3	275	4.1×10^{20}	143.6
22	5.50	10.72	3	253	5.4×10^{18}	107.6
23	0.078	0.128	1	183	5.5×10^{11}	-26.7
24	0.105	0.172	1	182	5.9×10^{11}	-26.0
25	0.23	0.38	1	189	1.7×10^{12}	-17.4
26	0.33	0.54	1	166	2.9×10^{10}	-51.1
27	0.53	0.88	1	155	4.6×10^9	-66.4
28	0.81	1.34	1	154	3.8×10^9	-68.0
29	1.18	1.97	1	149	1.8×10^9	-73.9

$> E_{Zn} = 1.6$. Thus, one again obtains agreement with the experimentally found thermal stability sequence for the copolymers.

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 most frequently found order of reaction for the main decomposition step of the investigated copolymers was equal to one, according with the common observation that the degradation of vinyl polymers usually follows first-order kinetics [10]. In the case of cobalt(II) and nickel(II)-containing copolymers, the increase of n with increasing metal content suggests a change in the mechanism of degradation. It is known [19] that similar reaction orders indicate the breaking of chemical bonds of the same energy, and in fact the same type of reaction.

The E_a value determined for PS in the present case is identical (within limits of error) with that obtained for PS by Anderson and Freeman [20]. In both cases the same sample weight of 100 mg was used. Other literature values of E_a for polystyrene [21] range from 163 to 306 kJ/mole.

The E_a values compared at a given reaction order reveal the same pattern of relationship to the composition of the copolymers under study as was observed for their thermal stabilities.

The positive and increasing ΔS values for A_2Zn -St copolymers indicate [6] that the activated complexes have less ordered structures than those of the reactants, at increasing metal contents in the copolymers. This increase in ΔS , though favourable for an enhanced rate of decomposition, is probably more than compensated for by the increase in the E_a values. Similar results were obtained [22] for the thermal decomposition of $KBrO_3$ catalysed by Al_2O_3 . For A_2Cu -St copolymers, only negative ΔS values are obtained; these become more negative with increasing copper content.

The values of the preexponential factor Z are found to be in the range 1.8×10^9 – 7.7×10^{21} and are comparable with those observed for the thermal decomposition of other compounds [6, 22, 23].

Conclusions

The temperature characteristics of the thermal degradation of some transition metal acrylate-styrene copolymers have been determined.

The observed thermal stability sequence for the copolymers, A_2Zn -St > A_2Co -St > A_2Ni -St > A_2Cu -St, correlates with those for the corresponding metal acrylates and polyacrylates. It also conforms with the electron-withdrawing power of the side-group attached to the carbon atom at which chain scission occurs.

The reaction orders are equal to one for all A_2Zn -St and A_2Cu -St copolymers studied, but for some A_2Co -St and A_2Ni -St samples higher reaction orders are also observed.

The sequence of activation energies of decomposition for the investigated copolymers is in agreement with their thermal stability sequence.

The changes in ΔS reveal that the entropy factor acts on the thermal degradation of the copolymers in the opposite direction to the E_a of that process.

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Zusammenfassung — Die Prozesse der thermischen Zersetzung von Kopolymeren von Styrol mit Zink-, Kobalt-, Nickel- und Kupferacrylat wurden thermogravimetrisch untersucht. Während die thermische Stabilität der Zink enthaltenden Kopolymere bei höheren Metallgehalten ansteigt, nimmt die der die anderen Metalle enthaltenden Kopolymeren ab, und zwar, abhängig vom Metall, in der Reihenfolge $\text{Co} > \text{Ni} > \text{Cu}$. Die kinetischen Parameter n , E_a , Z und ΔS wurden nach der Horowitz–Metzger-Methode bestimmt und einer näheren Betrachtung unterzogen. Hinsichtlich des Wertes von E_a ergibt sich die gleiche Reihenfolge der Kopolymeren wie für die thermische Stabilität. Der Entropiefaktor läßt eine thermodynamische Hemmung der Zersetzung von Kopolymeren geringer thermischer Stabilität und eine preferentielle Zersetzung der Kopolymeren hoher thermischer Stabilität vermuten.

Резюме — Методом ТГ изучены процессы термической деструкции и определены температурные характеристики сополимеров стирола с акрилатами цинка, кобальта, никеля и меди. Термическая устойчивость цинксодержащих сополимеров увеличивается с увеличением содержания металла, а термоустойчивость других металл-содержащих сополимеров уменьшается и изменяется в ряду $\text{Co} > \text{Ni} > \text{Cu}$. Кинетические параметры n , E_a и ΔS определялись по методу Хоровица–Метцера. Вычисленные значения E_a коррелируются с наблюдаемой термоустойчивостью сополимеров. Энтропийный фактор указывает на термодинамическую помеху в разложении сополимеров с низкой термоустойчивостью и предпочтительностью разложения сополимеров с высокой термоустойчивостью.