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A comparative study of the influence of Na(K)SCN and Na(K)I on the thermal stability and the flow characteristics of polyoxyethylene

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Abstract

A comparative study on the thermal behaviour and the flow characteristics of binary mixtures of Na(K)SCN and Na(K)I with polyoxyethylene (POE) within a broad temperature interval was conducted by means of a combined dynamic thermal analysis, gel permeating chromatography, dynamic viscometry, IR spectroscopy and an extrusion plastometer. The concentrations of the salts varied from 0.1 to 40 mass% and the mean viscosity molar mass ($\bar{M}_v$) of POE was found within 7×10^3–5.5×10^6 g mol^{-1} range.

The same optimum concentrations of the salts (2–5 mass%) were found to considerably improve the thermostability of POE in air and also its melt index. The thermostabilizing effect of the salts was achieved regardless of the molar mass of the POE and the way they were incorporated. The thermostability and the melt index of the POE increased in the order: KI, KSCN, NaSCN, NaI.

By employing a novel and appropriate experiment, solid-phase alkali metal salt was found to 'trap' the gaseous products of the primary decomposition of POE, thus forming the ionic complex and, also acting as an antioxidizing agent.

Keywords: Polyoxyethylene; Binary systems; Alkali salts; Thermostability; Flowing

1. Introduction

The thermostability of polyoxyethylene (POE) is known to increase in the presence of some inorganic salts, including the salts of alkali metals [1,2] by forming ionic complexes (IC) of high electroconductivity. The IC of POE with both Na(K)SCN and Na(K)I are comparatively well-known and have been studied [3–5]. The thermal behaviour of these systems in the solid state, however, was insufficiently explored [2,6–8]. In our previous study, very low concentrations of Na(K)SCN [7] and Na(K)I [8] were found to have a thermostabilizing effect on POE in air close to that of the IC containing much higher concentrations of the salts (35–40 mass%). Low concentrations of these salts caused a considerable increase of the melt indexes (MI) of high molar mass POE (HMPOE) [8,9]. A comparative evaluation and analysis of the data obtained, and also some new data, can be useful for clarifying the prevalent total mechanism and kinetics of the thermostabilizing effect of these alkali salts on POE and the corresponding influence ions. They can also be useful to the processing of HMPOE by moulding under pressure, extrusion, etc..

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The aim of the present work was to study and compare the influence of a wide range of concentrations of Na(K)SCN and Na(K)I on the thermal behaviour including the melt indexes of POE in a broad temperature interval.

2. Experimental

2.1. Starting materials

Binary systems of five types of POE with mean viscosity molar masses (in g mol^{-1}) ($\bar{M}_v$) varying from 7×10^3 to 5.5×10^6, denoted by POE_1 ($\bar{M}_v = 1.8 \times 10^6$), POE_2 ($\bar{M}_v = 2 \times 10^4$), POE_3 ($\bar{M}_v = 7 \times 10^3$), POE_4 ($\bar{M}_v = 3.2 \times 10^6$) and POE_5 ($\bar{M}_v = 5.5 \times 10^6$), were analysed [7–9]. The HMPOE-es – POE_1, POE_4 and POE_5 are commercial products of 'CHIMIC' (Dimitrovgrad, Bulgaria), POE_2 is a commercial product of 'VERILA' (Sofia, Bulgaria) and POE_3 of 'MERCK' (Germany).

KSCN, NaI and KI (p.a.), commercial products of 'REACHIM' (Ukraine), and NaSCN (p.a.), commercial product of 'CHEMAPOL' (Praha, Czech Republic), were used. Their concentrations in the mixtures varied from 0.1 to 40 mass%. Binary mixtures were prepared in three ways [7,9].

2.2. Methods

2.2.1. Thermoanalytical methods

For obtaining TG, DTG and DTA curves, a combined dynamic thermal analysis apparatus, an OD-102 derivatograph (MOM, Budapest), was used under the following conditions: heating rate 6 K min^{-1}, sample initial mass in all the experiments 0.1 ± 0.00005 g in the form of powder or foil kept in the presence of drier: holder, a Pt crucible ϕ9.5 mm; thermocouples Pt/PtRh; no standard substance; medium, air (static) and nitrogen flowing over the sample at a rate of 17 l/h. Using the TG and DTG curves, the effective activation energy of the thermal decomposition (E_a) of the samples under study was determined [10,11]. Through graphical integration, by the weight method, the areas of the total exothermal peaks of the oxidative decomposition were measured and calculated for 100% thermoactive component (ΔQ, %).

2.2.2. Gel permeating chromatography (GPC)

The binary mixtures were treated under isothermal conditions at 150°C for 20 h in air medium. The average number molar mass (MM), $\bar{M}_n$, average weight MM, $\bar{M}_w$, and molar mass distribution (MMD) before and after the thermal treatment of POE and its binary mixtures containing 2 and 5 mass% inorganic salts were determined by GPC. For this purpose an LKB Bromma 2150 HPLC (WATERS) equipped with an RL 401 differential refractometer as a detector, a PL gel $5\mu\times10^3$ column, chloroform as a solvent, polystyrene as a standard calibrating substance and processing program MAXIMA 820 were used.

2.2.3. Dynamic viscometry

The dynamic viscosity before and after the thermal treatment (at 150°C for 20 h) of POE_1 and its mixtures with KI (1–10 mass%), and POE_3 and its mixtures with NaSCN (0.5–5 mass%) was measured by means of a Reotest-2 rotation viscometer. A cylindric measuring device with cylinders S/S_1 was used. For the analysis, 0.5% solution of the binary mixture in distilled water were prepared and allowed to stay for 24 h. Just before viscosity measurements, each solution was agitated in a shaking device for 1 h. The dynamic viscosity (η) at 30°C and the viscosity decrease, $\Delta\eta$ %, after thermal treatment compared with that of the corresponding mixture before thermal treatment were determined.

2.2.4. IR spectroscopy

IR spectra of foils of the initial POE (chloroform) and of the IC (methanol) were obtained by means of an IR-spectrometer 'Specord M80', Germany.

2.2.5. Flow measurement (MI)

MI of binary mixtures, containing 2 and 5 mass% of alkali salts were made by means of an extrusion plastometer meeting the requirements to ASTM-1238-65 T at loading P-21.6 kg, sample mass 4 g and residence time 4 min, at 200, 250, 265 and 280°C. The MI at 200°C of mixtures which had been passed through the extruder at the above temperatures (secondary MI) was also determined.

3. Results and discussion

3.1. Comparative thermal investigations

It was found that Na(K)SCN and Na(K)I form IC with POE of the following melting temperatures (T_m): T_m of the IC of 190–200°C for IC of NaSCN and NaI; 110°C for IC of KSCN; the IC of KI was amorphous [3–5]. All these IC have considerably higher thermostability in air medium than that of the initial POE. In previous investigations [7–9], we have found that low concentrations of these salts change to a significant degree the pattern of the thermal curves of POE in air medium. Some of the typical results are presented here too. At very low concentrations of the salts in the binary mixtures (0.1–5 mass%) the initial temperatures of oxidation (T_{ox}) and mass release ($T_{0\%}$) increase considerably as compared with those of the initial POE$_I$ (Figs. 1 and 2). These two temperatures were almost the same and corresponded to the induction period (τ_{ind}) established from the beginning of the first exothermal peak on the DTA curves [8]. The increase of the salt concentration resulted in a higher initial temperature of decomposition ($T_{0\%}$) and temperature of 10% decomposition ($T_{10\%}$) by 130 and 100°C, respectively. The temperature of 50% decomposition ($T_{50\%}$) increased, by ca. 40°C only (Fig. 2), whereas the temperature of the maximum decomposition rate (T_{max}), increased by ca. 10°C [7–9]. The higher alkali salt content, led to a higher thermostability [7]. The effective E_a of the basic thermooxidative decomposition also increased (Fig. 3) [7].

Beside the considerable shift towards higher temperatures, a certain reduction in the initial exothermal peaks of POE oxidation was also observed. As the content of the salt was 2–5 mass%, the first exothermal peaks vanished almost completely, and there was sharp reduction in the others. At the same time the general heat release and the areas of the exothermal peaks, $\Delta Q\%$, were reduced by more than 50% in comparison with those for the initial POE$_I$ (Fig. 4) [7].

As the content of NaI, NaSCN and KSCN was more than 5 mass%, a separate stage appeared in the de composition of the by-product formed after the basic decomposition of the samples (Fig. 1, curves 3 and 4).

The thermal behaviour of both the mixtures containing 2–5 mass% of the alkali salts and their IC containing 35–40 mass% of the salts in air, were similar to the initial POE in an inert medium (Fig. 1).

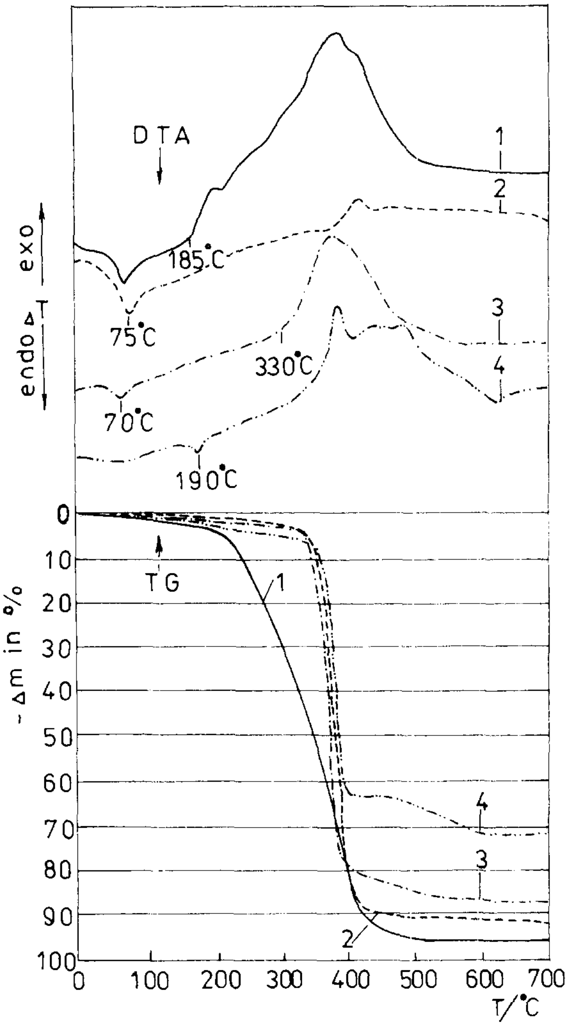

Fig. 1. Measured curves of POE$_I$ in air (curve 1) and in nitrogen (curve 2); mixture of POE$_I$ and 5 mass% NaI (curve 3); ionic complex of POE$_I$ and NaI (curve 4).

Regardless of $\bar{M}_v$ of POE in the binary mixtures, the resulting thermostabilizing effect of the salts was of the same order and exhibited a similar mechanism [7,8]. This effect was independent from the mode of introducing the salts into POE [7]. It should also be noted that for the mixtures of POE and KI no other high-temperature step of the decomposition was observed. This was found to be true for the IC, too. The decrease in the heat release was observed at

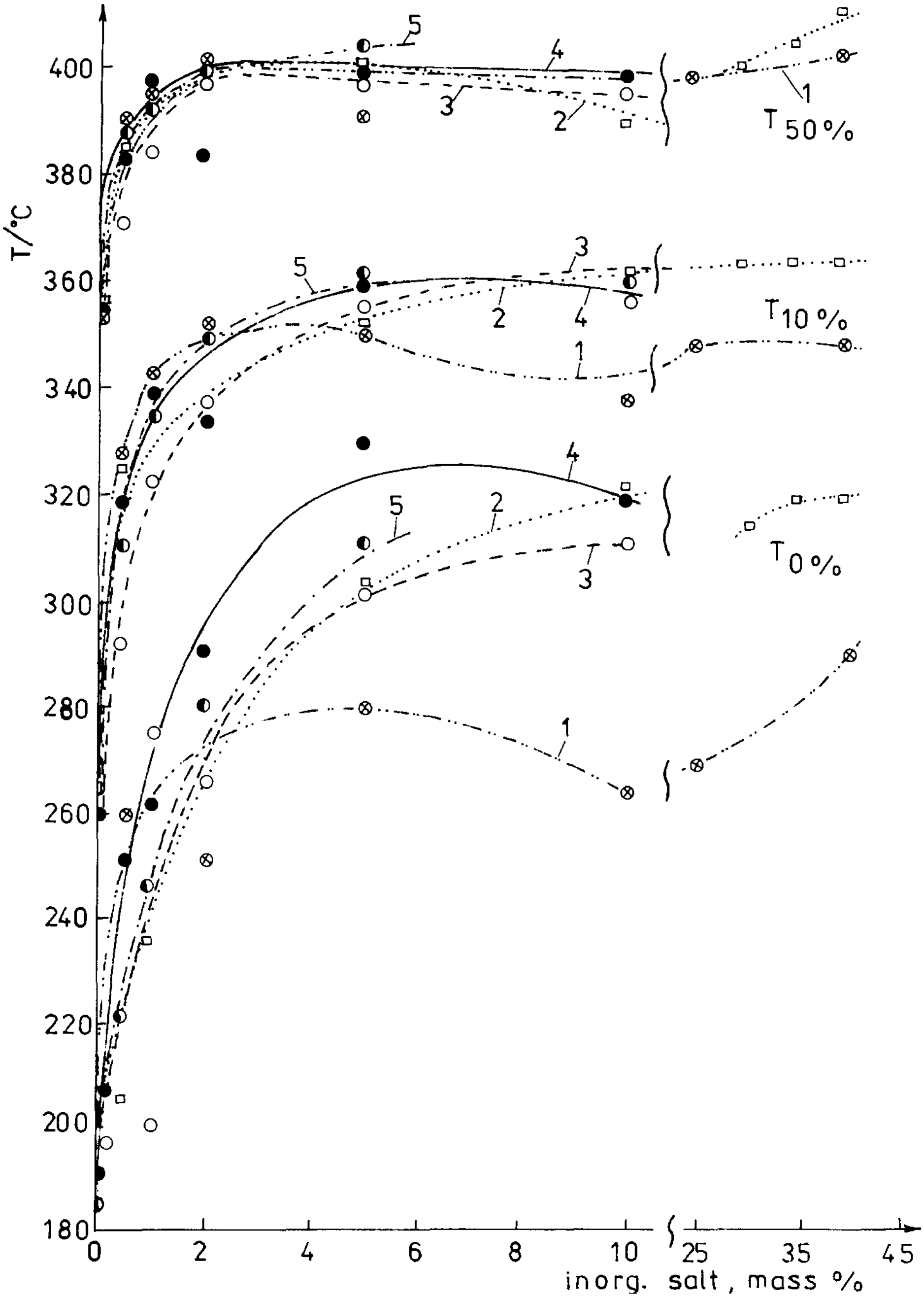

Fig. 2. Thermal characteristics ($T_{0\%}$, $T_{10\%}$ and $T_{50\%}$) of the binary mixtures of POE_1 and POE_2 and alkali metal salts; (1) mixtures of POE_1 with KI; (2) mixtures of POE_1 with KSCN; (3) mixtures of POE_1 with NaSCN; (4) mixtures of POE_1 with NaI; (5) mixtures of POE_2 with NaI.

temperature below 300°C only. After that, the amount of heat released was sufficient to catalyse the burning of the polymer almost completely at about 450°C. As the IC of POE and KI was heated, a mass loss was observed after the moisture release but before the start of the basic decomposition of the sample. This mass

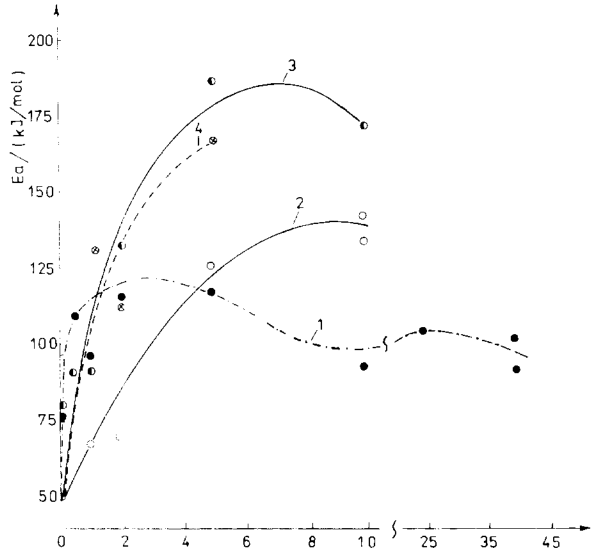

Fig. 3. Dependence of the E_a of the thermal decomposition of binary mixtures of POE_1 and POE_2 with alkali salts on the salt content: (1) mixtures of POE_1 with KI; (2) mixtures of POE_1 with NaSCN; (3) mixtures of POE_1 with NaI; (4) mixtures of POE_2 with NaI.

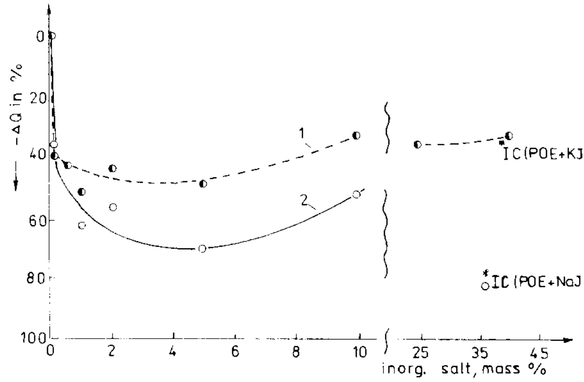

Fig. 4. Decrease of the total heat release by thermooxydative decomposition (ΔQ, %) of the binary mixtures of POE_1 and KI (curve 1), and POE_1 and NaI (curve 2).

loss could also be accounted for by the formation on low-molecular fragments. They cannot recombine because of the amorphous structure of the IC of POE and KI unlike IC of the other salts whose crystalline structure favours a recombination of the free radicals.

The present thermal analysis data and those from our former studies [7–9] can be used to compare the thermostabilizing effects of these salts on POE in air medium. It can be seen that NaI and NaSCN are more effective than the potassium salts. This difference is more pronounced with iodides than with thiocyanates. The most probable reason for these slight differences may be the stability of their IC with POE. Whereas T_m of IC with the sodium salts was between 190 and 200°C and T_m of IC with KSCN was between 90 and 115°C, IC with KI was found to be amorphous and softened at ca. 70°C. It is well-known that the polymers are more susceptible to oxidation in a molten state than in solid phase.

3.2. GPC and dynamic viscosity investigations.

The results from the determinations of MM and MMD by the method of GPC of heated mixtures of POE_3 and alkali salts with detected concentrations, compared with those for the initially heated POE_3 (Table 1, Fig. 5) confirm the thermostabilizing effect of the alkali salts on POE_3. The $\bar{M}_n$ of heated pure POE_3 gets decreased by more than 70% in comparison with the non-heated POE_3. The range of the decrease in $\bar{M}_n$ and $\bar{M}_w$ of the binary mixtures under study was several times lower. In some cases (e.g. with samples of 5 mass% NaI, and 2 or 5 mass% NaSCN), these characteristics remained almost unchanged. Mixtures containing KI, have a lower MM. Polydispersity of the thermally treated pure POE_3 increased by about 130%, whereas no such changes were observed with the mixtures. The mixtures of POE_3 with the thiocyanates had higher polydispersity than the corresponding mixtures with iodides, which may be due to the higher volatility of the latter.

The preliminary data obtained at this stage concerning the change in the dynamic viscosity of heated binary mixtures of POE_1 and KI (Fig. 6, curve 1), and of POE_5 and NaSCN (Fig. 6, curve 2) show that increasing the concentration of the alkali salt up to 5 mass%, weakened the trend of decreasing the viscosity of the aqueous solutions of thermally treated mixtures of POE. At concentrations of the salt above 5–10 mass% the decrease in the viscosity did not depend substantially on its concentration, which also confirmed the previous data for the thermostabilizing effect of these salts on the POE [7–9].

Table 1
Change of the molar mass and molar mass distribution of POE and its binary mixtures after thermal treatment

System	Inorg. salt cont. mass%	$\bar{M}_{n*}$	$\bar{M}_{w*}$	MMD
POE_3 – before heating	0	7211	7714	1.07
POE_3 – after heating	0	2056	5054	2.46
POE_3+NaI	2	6341	7129	1.12
POE_3+NaI	5	7531	8189	1.09
POE_3+KI	2	6063	6856	1.13
POE_3+KI	5	6796	7523	1.11
POE_3+NaSCN	2	6674	7945	1.19
POE_3+NaSCN	5	6642	7759	1.17
POE_3+KSCN	2	6202	7428	1.20
POE_3+KSCN	5	6994	7873	1.13

$\bar{M}_{n*}$, $\bar{M}_{w*}$ – average number (weight) molar mass.

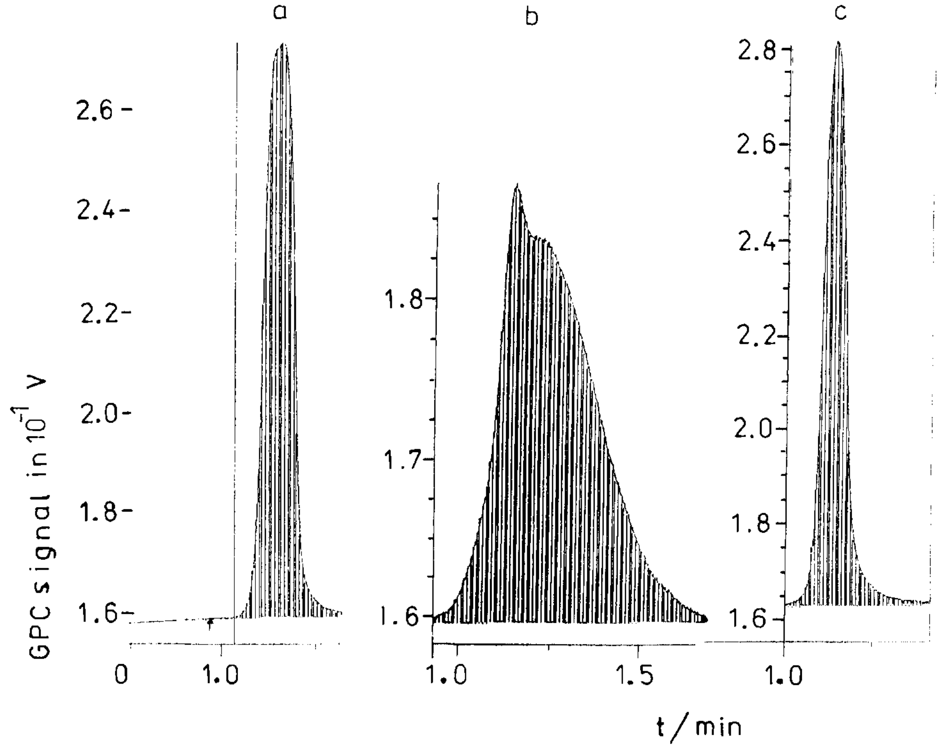

Fig. 5. (A) Chromatograms (GPC) of the initial POE_2; (B) POE_2 heated at 150°C for 20 h in air; (C) mixture of POE_2 : NaI (95 : 5 mass%), heated at 150°C for 20 h in air.

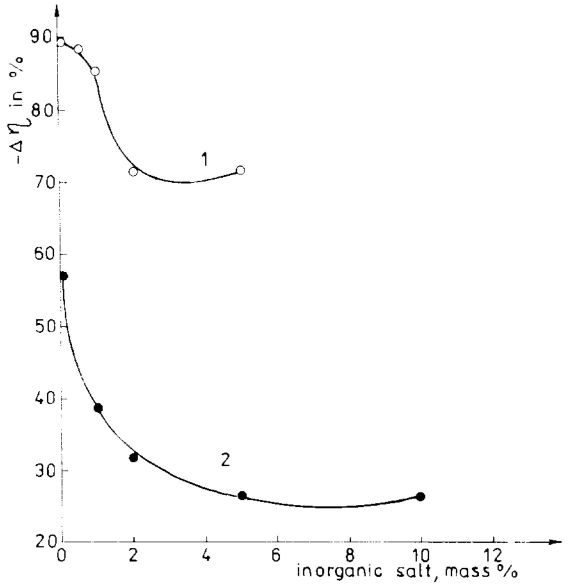

Fig. 6. Decrease of the dynamic viscosity η of the aqueous solutions of the thermally treated mixtures of (1) POE_1 and KI and (2) POE_3 and NaSCN, depending on the concentration of inorganic salts.

3.3. *On the prevalent total mechanism of the thermostabilizing effect*

To clarify the nature and the total mechanism of the thermostabilizing effect of the alkali salts on POE in air medium, a novel and appropriate experiment was carried out. Its scheme is shown in Fig. 7. 0.062 g of POE_1 were weighted out in a crucible for analysis. A fine metal net was fixed at a certain distance from the POE_1. 0.038 g of NaSCN were sprinkled over the net without having a direct contact with POE_1. In this case the ratio between POE_1 and NaSCN was equal to that of their IC. The analysis was conducted in air medium.

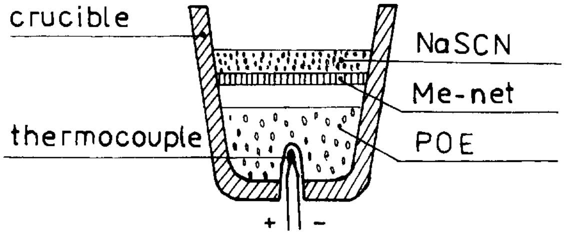

Fig. 7. A scheme of a novel experiment by means of a derivatograph.

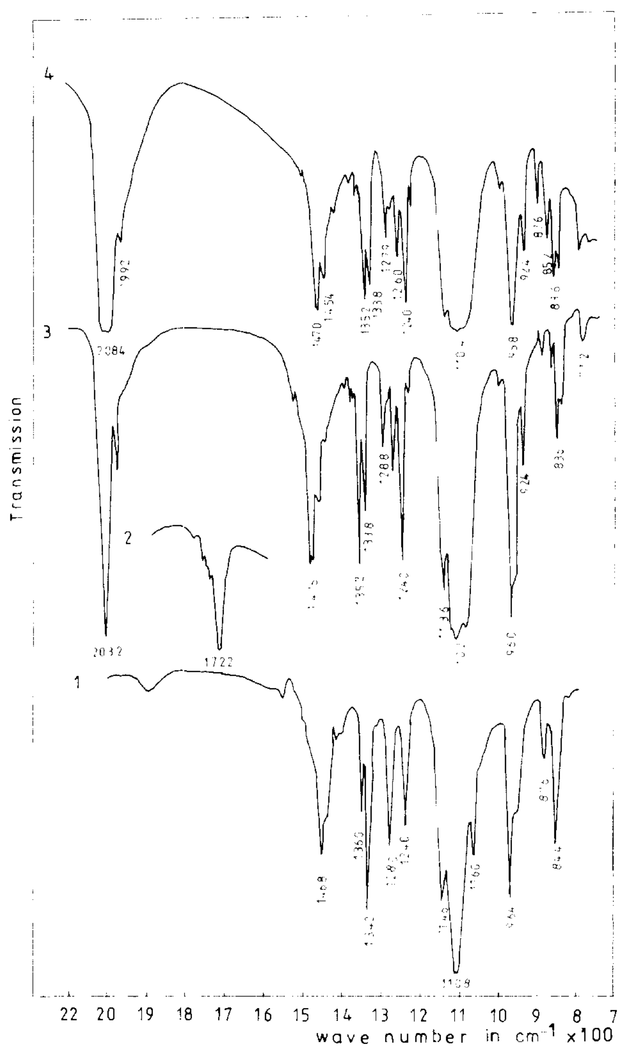

Fig. 8. IR spectra of foils heated at 200°C: (1) POE_3 (chloroform), heated in nitrogen; (2) POE_3 (chloroform), heated in air; (3) IC of POE_3 and NaSCN (methanol), heated in air; (4) the product obtained over the Me-net (methanol), heated in air (see Fig. 7).

If the experiment was conducted up to 200°C (T_{melt} of IC) and the IR spectrum after heating the product obtained over the net was recorded (Fig. 8, curve 4), this would be the spectrum of the IC of POE and NaSCN (Fig. 8, curve 3). If the experiment was performed at 600°C, the TG curve obtained would be similar to that of the IC of POE and NaSCN and the thermostabilizing effect would be also observed (Fig. 9, curve 2, 2′ and 2″). This effect was not observed if, instead of NaSCN, Al_2O_3 or another inert

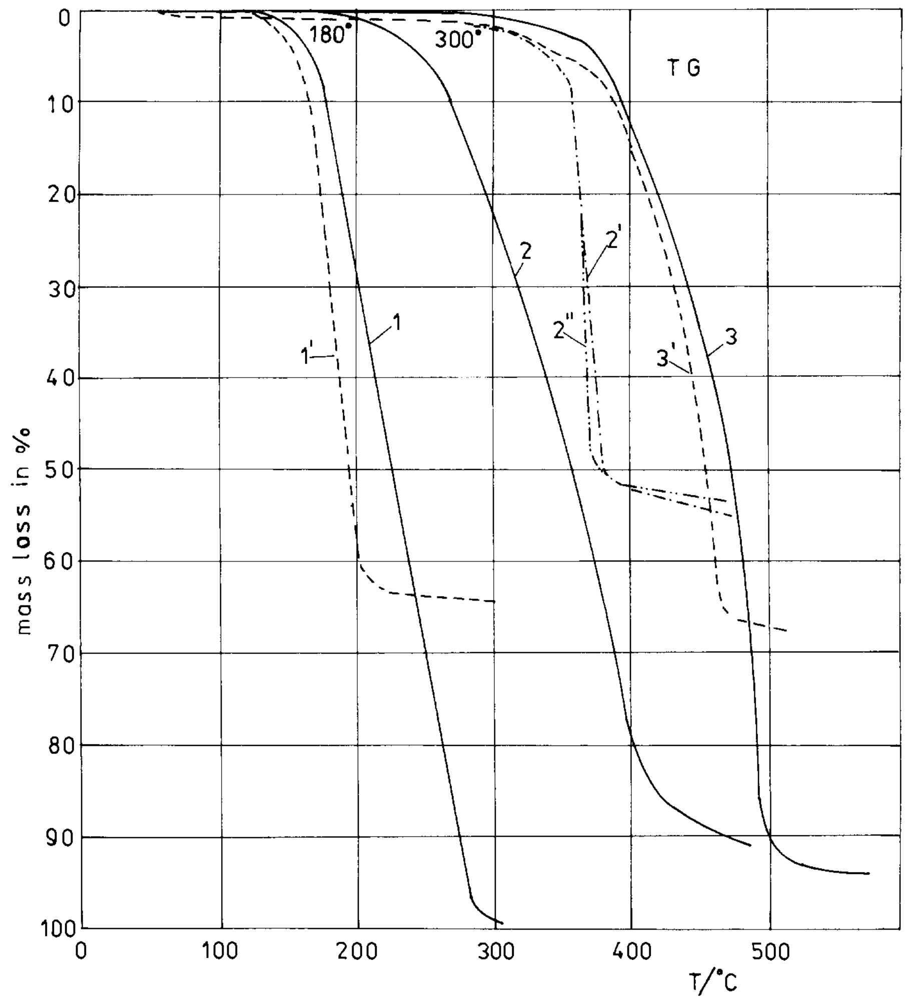

Fig. 9. TG curves of polyoxymethylene (POM), POE_3 and Polyethylene of low density (PELD) and their systems with NaSCN, registered in air according to the experimental given in Fig. 7. (1) POM; (1′) POM, mixed with 38 mass% NaSCN; (2) POE_3; (2′) POE mixed with 38 mass% NaSCN(IC); (2″) the product, obtained over the Me-net (see Fig. 7); (3) PELD; (3″) PELD, mixed with 38 mass% NaSCN.

substance was placed over POE. This is also true with polyoxymethylene (Fig. 9, curves 1 and 1′) or polyethylene (Fig. 9, curves 3 and 3′), which do not form complexes with alkali salts. Therefore, NaSCN over the net was found to ‘trap’ the primary gaseous products of the decomposition of POE, forming the IC. NaSCN also acts as an antioxidizing agent since in the spectrum of the IC formed over the net no absorption band at 1772 cm^{-1} (vs; C=O), which is characteristic of the spectrum of the initial POE_1 heated at 200°C in air medium (Fig. 8, curve 2) was observed. This band did not exist as a nitrogen medium instead of air was employed (Fig. 8, curve 1).

Further investigations are to be conducted aiming at studying the possibility of alkali salts taking part in expected secondary chemical processes such as cross-linking, elimination, etc. over the higher temperature range.

3.4. Comparative study of the melt indexes

The results from the study of the MI reveal interesting behaviour of these mixtures as far as the

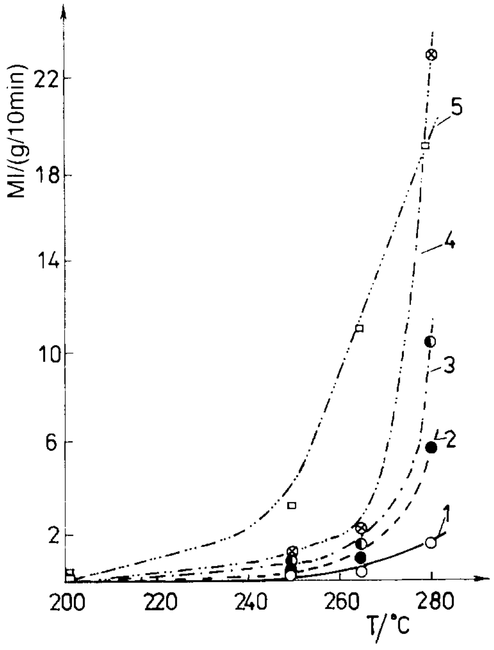

Fig. 10. Dependence of the MI of the binary mixtures of HMPOE (POE_5) and alkali salts (conc. 5 mass%) on the temperature of extrusion: (1) POE_5; (2) mixtures with KI; (3) mixtures with KSCN; (4) mixtures with NaSCN; (5) mixtures with NaI.

requirements for their thermostability and processability are concerned. The MI of the initial HMPOE-1 is very low, and only at 280°C and maximum loading it exceeds 1 g/10 min (Fig. 10, curve 1). After second extrusion at 250°C and maximum loading, the MI of HMPOE-1 is about 1 g/10 min (Fig. 11, curve 1). However, the thermal characteristics showed that, long before these temperatures were attained, the initial POE had decomposed to a considerable extent. This is why, the initial HMPOE cannot be processed by moulding under pressure and extrusion. In the presence of (2–5 mass%) the alkali salts the melt flow of HMPOE increased substantially. The degree of increasing the MI is the highest with the mixtures of NaI, and the lowest with the mixtures of KI (Figs. 10 and 11, curves 2 and 5). With increasing the temperature, the degree of increasing the melt flow of the mixtures of NaSCN is slightly higher than that of the mixtures of KSCN (Figs. 10 and 11, curves 3 and 4).

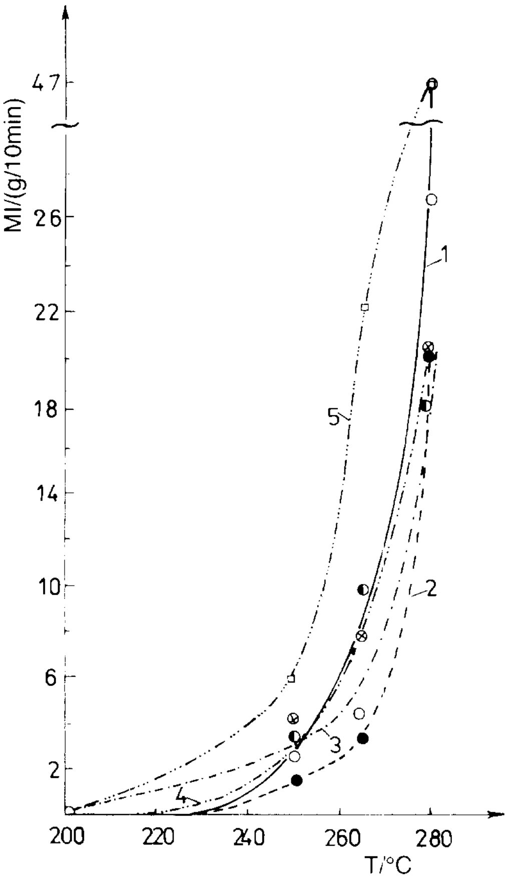

Fig. 11. Dependence of the secondary MI of the binary mixtures of HMPOE (POE_5) and alkali salts (conc. 5 mass%) on the temperature of secondary extrusion: (1) POE_5; (2) mixtures with KI; (3) mixtures with KSCN; (4) mixtures with NaSCN; (5) mixtures with NaI.

The considerable increase in the thermostability of the mixtures and their flow characteristics are important advantages in their processing into manufactured articles.

4. Conclusions

1. By means of thermoanalytical methods, GPC, dynamic viscometry and IR spectroscopy, it was found that the alkali salts, introduced in optimum minimum concentrations of 2–5 mass%, have a considerable thermostabilizing effect on the total as well as the molar mass and molar mass distribution of the POE in air medium. This effect

was achieved regardless of the molar mass of POE and no matter how the salts were introduced into it.

2. The thermostabilizing effect of the alkali salts studied increases in the order: KI, KSCN, NaSCN, NaI. It was suggested that this effect depends on the stability of their ionic complexes with POE.
3. By conducting a novel and appropriate experiment the solid-phase alkali metal salt was shown to 'trap' the gaseous products of the primary decomposition of POE forming the ionic complex and also acts as an antioxidizing agent.
4. It was found that the alkali salts, introduced in the same optimum minimum concentrations (2–5 mass%), considerably improve the melt flow of HMPOE. The melt indexes increase in the same order as mentioned for the thermostabilizing effect: KI, KSCN, NaSCN, NaI.

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