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THERMAL INVESTIGATION OF INHIBITION OF POLYBISMALEIMIDE POLYMERIZATION

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DTA and DSC data revealed that the use of heteropoly compound additives allows an increase in the temperature of polybismaleimide radical polymerization by 20–60 deg in comparison with the value for the initial olygomer. TG data showed that in the presence of certain amounts of the inhibitor the polymer thermoresistance does not decrease. The range of effective concentration of the inhibitor is 1–5 wt.%.

The attempts to increase the technological effectiveness of synthesis and reprocessing of heterocyclic polymers has stimulated a new tendency, viz. the synthesis of low-molecular oligoimides, fusible and soluble in organic solvents, having end-functional groups or multiple bonds capable of polycondensation or polymerization under definite conditions.

The most interesting of them are polybismaleimides (PBMI), which form the basis of industrial polymer material [1, 2] production in some countries. The comparatively low melting point (80–120°) of PBMI allows their application as thermoresistant impregnated and poured compounds. However, the presence of multiple carbon-carbon bonds, leading to the formation of cross-linked structures, promotes a rapid increase in melt viscosity, which hampers product manufacture. It is not a solution to prolong the time of melt viability by the traditional method of inhibition of polymerization through quinone [3] application, and the addition of considerable quantities of inhibitor results in deterioration of the polymer thermoresistance.

It is well known that metals with variable valency, and Fe^{3+} in particular, being electron donors, are capable of inhibiting vinyl monomer [4] polymerization.

Hence, it was of interest to study the possibility of inhibiting the PBMI polymerization process by using heteropoly compounds (HPC) that are polynu-

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clear complexes, having Mo(VI), W(VI) and V(V) in their composition. A high redox potential, strong acidity, thermal stability and good solubility in organic media are their advantages over certain other inhibitors.

Experimental

Materials

Polybismaleimide (TU–09–06–143–73) was obtained by migratory copolymerization of 4,4′-diphenylmethane-N,N′-bismaleimide with 4,4′-diaminodiphenylmethanol, with the reacting components in a ratio of 4 : 1.

Heteropoly compounds with the common formula $XM_{12}O_{40}^{x-8}$ or $XM_{12-n}V_nO_{40}^{x-n-8}$, where X = Si or P, and M = Mo or W, were obtained by reported methods [5, 6].

The compositions PBMI + HPC were prepared by dry-mixing the initial components in a mechanical disperser at 900 r.p.m. The HPC were previously subjected to thermal treatment in the temperature range of their stability. The crystal water quantity did not exceed 6–8 moles per mole of HPC, which did not greatly influence the polymerization process. The total HPC content varied from 0.5 to 10% of the polymer weight.

Apparatus

A derivatograph (MOM) was used for the thermal investigations (TG and DTG) at a heating rate of 5 deg min^{-1} with 100 mg weighed amount in air or argon. DSC curves were recorded by means of a differential scanning calorimeter (DuPont), at a heating rate of 10 deg min^{-1}, with 20 mg weighed amount in helium.

The polymerization process was tested via the gel fractions produced, through extraction of the reaction mass with N,N′-dimethylformamide in a Soxhlet apparatus for 20 h. The residue was dried to constant weight at 100–200 Pa and 60°.

Results and discussion

The DTA and TG curves of the initial PBMI and of compositions containing different HPC quantities are presented in Figs 1 and 2. The results (curves a) show that the thermooxidative destruction of the initial polymer is accompanied by the loss of volatile matter and a large endothermic effect at 300–400°. At lower temperatures an appreciable change in the sample mass is not observed, but the DTA curve has a complex character; this is connected with the processes of phase

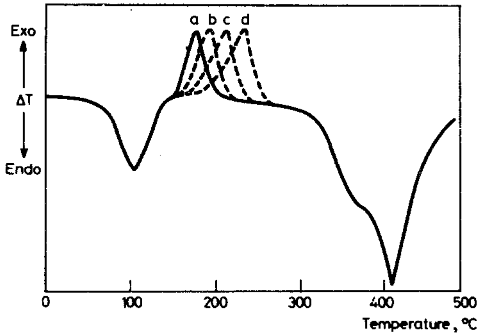

Fig. 1 DTA curves of a) PBMI; b) PBMI + 2% $H_4SiW_{12}O_{40}$; c) PBMI + 2% $H_3PMo_{12}O_{40}$; d) PBMI + 2% $H_6PMo_9V_3O_{40}$

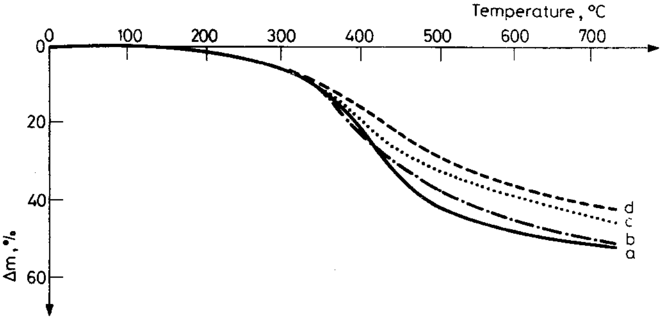

Fig. 2 TG curves of a) PBMI; b) PBMI + 0.5% $H_3PMo_{12}O_{40}$; c) PBMI + 2% $H_3PMo_{12}O_{40}$; d) PBMI + 5% $H_3PMo_{12}O_{40}$

transitions and polymerization. The endothermic effect at 110° corresponds to the phase transition of the first order PBMI → melt. The multiple bond polymerization is reflected in the exothermic effect at 180°.

HPC addition does not cause essential changes in the TG results (Fig. 2). At the same time, DTA (Fig. 1, curves b, c, d) reveals a shift in the polymerization temperature maximum (ΔT) by 20–60 deg for compositions containing HPC in comparison with the value initial for the PBMI. The inhibition of PBMI polymerization takes place above an HPC content of 0.5% by weight. The maximum ΔT is observed at 2–5% of HPC by weight. A further increase of the inhibitor quantity has practically no influence.

From the TG results on the initial PBMI and its compositions with HPC in atmospheres of argon and air (Fig. 3) it can be seen that the thermal stability is higher in the inert atmosphere.

The DSC data in helium are identical with the DTA results in air, though the ΔT of polymerization is lower.

Table 1 Gel fraction yield by PBMI polymerization in melt at 180 ± 5 °C

Time of polymerization, min	Gel fraction yield (wt.%)		
	PBMI	PBMI + 2% $H_6PMo_9V_3O_{40}$	PBMI + 2% $H_3PMo_{12}O_{40}$
30	31.9	20.6	19.7
60	33.1	23.6	24.3
90	51.1	25.5	42.5
120	72.7	57.7	60.6

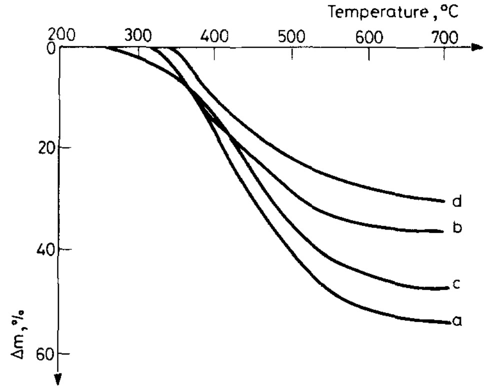

Fig. 3 TG curve a) PBMI (air); b) PBMI (argon); c) PBMI + 2% $H_4SiW_{12}O_{40}$ (air); d) PBMI + + 2% $H_4SiW_{12}O_{40}$ (argon)

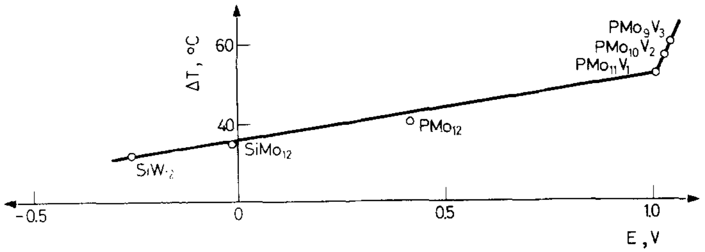

Fig. 4 Dependence of HPC redox potential on the temperature rise of polymerization

The shift in the exothermic effect of polymerization to higher temperature correlates well with the literature data on HPC redox potentials [7]. The HPC oxidative potential increases linearly with the ΔT of polymerization (Fig. 4). In the case of HPC containing vanadium, $PMo_{12-n}V_n$, this linear regularity is not observed. This can increase in the number of reduced vanadium atoms. Thus, the

ΔT of polymerization rises from 45 to 60 deg as the vanadium content increases from 1 to 3.

Together with the thermal analysis data, these results testify to the fact that the mechanism of PBMI inhibition seems to be explained by the high electron-donor properties of HPC, which are easily converted by reduction into complexes of mixed valency.

The viability of the initial PBMI melt and of a composition containing 2% of HPC by weight was determined via the gel fraction yield. As seen from the data in Table 1, the gel fraction quantity is lower in the presence of HPC. The best results were achieved with $H_6PMo_9V_3O_{40}$, which accords with the thermal analysis data.

Thus, the results of the thermal investigation testify to the inhibition of the PBMI polymerization reaction by heteropoly acids, without any deterioration in thermal stability. The range of effective concentration of the inhibitor is 1–5 wt.%.

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Zusammenfassung — Nach DTA und DSC-Befunden kann die Anwendung von Zusätzen von Heteropolyverbindungen die Polymerisationstemperatur um 20–60° erhöhen. Nach TG-Ergebnissen nimmt die Wärmebeständigkeit des Polymers in Gegenwart kleiner Inhibitormengen nicht ab. Der Inhibitor wirkt in einer Konzentration von 1–5 Gew.%.

Резюме — Согласно данным ДТА и ДСК, использование в качестве добавок гетерополисоединений приводит к повышению температуры радикальной полимеризация полибисмалеинимида на 20–60° по сравнению с исходным олигомером. Согласно же данным ТГ, наличие небольших количеств ингибитора не вызывает уменьшения термоустойчивости полимера. Концентрация ингибитора в 1–5 весовых процента является наиболее эффективной.