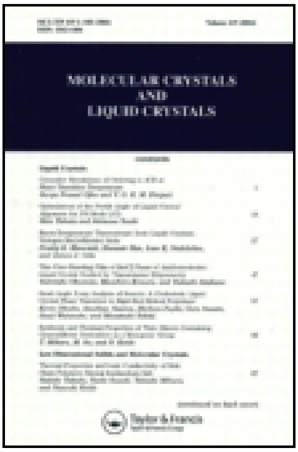

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Investigation of Inhibiting Action Mechanism of Succinimidophenylmethacrylate Derivatives Prepared by the Diels-alder Reaction on Polystyrene Decomposition

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Investigation of Inhibiting Action Mechanism of Succinimidophenylmethacrylate Derivatives Prepared by the Diels–Alder Reaction on Polystyrene Decomposition

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The influence of succinimidophenylmethacrylate derivatives on the polystyrene thermal stability in argon is assessed by dynamic thermogravimetric analysis. The monomers (1 or 3 mol%) prepared by Diels–Alder reaction have been introduced into polystyrene by means of the copolymerization reaction. The decomposition products of polystyrene with additions have been investigated by thermal desorption analysis coupled with mass spectrometry. During the heating of polystyrene with additions, the retro-Diels–Alder reaction produces dienes and dienophiles which react with macroradicals and thus inhibit the radical chain process of polymer thermal decomposition. The inhibiting effect of the succinimidophenylmethacrylate derivatives is determined by the temperature range of the retro-Diels–Alder reaction.

Keywords Copolymerization; diene; dienophile; inhibitor; polystyrene; succinimidophenylmethacrylate derivative

Introduction

Polystyrene (PS) is a large-volume commercial polymer used in a variety of applications. Recently [1–3], we have reported the antioxidant action of a number of imidophenylmethacrylates which have been built in a polystyrene macromolecular chain by means of the copolymerization reaction. Such a technique is possible when components are copolymerized and allows achieving the perfect molecular distribution of an antioxidant and excluding its undesirable weep and volatility [4,5]. Later on [6], it was ascertained that some of the studied additions possess also the inhibiting effect on PS decomposition in the argon atmosphere. The scope of this paper is the investigation of capabilities of succinimidophenylmethacrylate derivatives prepared by the Diels–Alder reaction [7] to enhance the resistance of PS against the radical chain process of decomposition in

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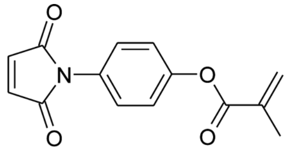
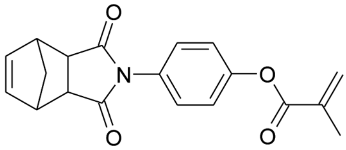
the inert atmosphere and to study some chemical aspects of the inhibiting action mechanism of these compounds.

Experimental

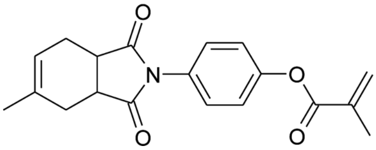
The succinimidophenylmethacrylate derivatives have been prepared by the methacrylation of Diels–Alder reaction products obtained from the corresponding dienes and p-maleimidophenol. Maleimidophenylmethacrylate was investigated for comparison, because it contains the same molecular fragment as that in applied succinimidophenylmethacrylate derivatives. The structures of maleimidophenylmethacrylate (p-MAPMA) and succinimidophenylmethacrylate derivatives such as p-methacryloiloxy-phenylimide-bicyclo-[2,2,1]-5-heptene-2,3-dicarbonic acid (p-endikimidophenylmethacrylate; p-ENDPMA) and 4-(5-methyl-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-isoindol-2-yl)phenyl-2-methylacrylate (p-MTGFTIPMA) are illustrated with the following structural formulas:



p-MAPMA



p-ENDPMA



p-MTGFTIPMA

Polystyrene and its copolymers with 1 or 3 mol% of the mentioned monomers were synthesized by the radical copolymerization with styrene (Aldrich) thermally initiated with azo-bis-isobutyronitrile (AIBN) (1 wt.%) at 78°C for 20 h.

Thermogravimetric experiments of the investigated samples were recorded on a TA Q 600 STD (TA Instruments). The thermal behavior of PS with and without additions was studied by DSC with the help of a Du Pont DTA/DSC-910 on a Du Pont 1090 thermo-analyzer. All measurements have been performed in the temperature range 20–650°C and a heating rate of 5°/min in the argon atmosphere. Weights of all the prepared polymer samples in use were 5–10 mg. The weight loss and the weight loss rate were recorded simultaneously. The temperature of the maximum rate of weight loss ($T_{\max}$) and the temperatures which correspond to 5, 10, and 40% of weight loss ($T_{5\%}$, $T_{10\%}$, and $T_{40\%}$) have been determined from the experimental data. The thermal decomposition products of the obtained samples have been investigated by the thermal desorption method in the temperature range 20–800°C, at a heating rate of 10°/m, and at a pressure of 10^{-6} Pa. The identity of desorbed particles was determined by mass spectrometry using an MX–7304A instrument.

Results and Discussion

The weight loss curves (TG) recorded as a function of temperature in argon for polystyrene and its samples with 3 mol% of maleimidophenylmethacrylate and succinimidophenylmethacrylate derivatives are presented in Figure 1. The results of DSC analysis are illustrated in Figure 2. The thermal behavior of PS suggests the pyrolytic polymer decomposition in a one-step reaction with endothermic feature. The thermal decomposition behavior of PS samples with additions is relatively simple. But all of the applied additions reveal some inhibiting effect on the PS decomposition. The weight loss for PS, PS-p-MAPMA, and PS-p-ENDPMA begins at 278°C (Fig. 1). The thermal decomposition for PS-p-MTGFTIPMA started at the temperature by about 31°C higher than that for PS (Fig. 1). So p-MTGFTIPMA inhibits the thermal decomposition of PS just at the beginning of this process. The additions p-MAPMA and p-ENDPMA start to reveal the inhibiting effect toward PS only at 306°C (Fig. 1). Comparing the temperatures $T_{5\%}$ and $T_{10\%}$, one can obtain the following order of the inhibiting effectivenesses of the studied additions: p-MAPMA, p-ENDPMA, and p-MTGFTIPMA (Table 1). The values of temperature of 40% weight loss ($T_{40\%}$), and temperature of the maximum rate of weight loss (T_{max}) for all applied additions have been registered to be not much different and are by several degrees higher than those for addition-free PS (Table 1). So p-MAPMA and succinimidophenylmethacrylate derivatives reveal the different inhibiting effects toward PS only on the initial stage of the polymer thermal decomposition. In the DSC analysis in argon stream (Fig. 2), PS samples with additions give the same endothermic peaks, whose minimum bottom appeared at the temperature about 12°C higher than that for polystyrene. We note that the decrease of the amount of an addition to

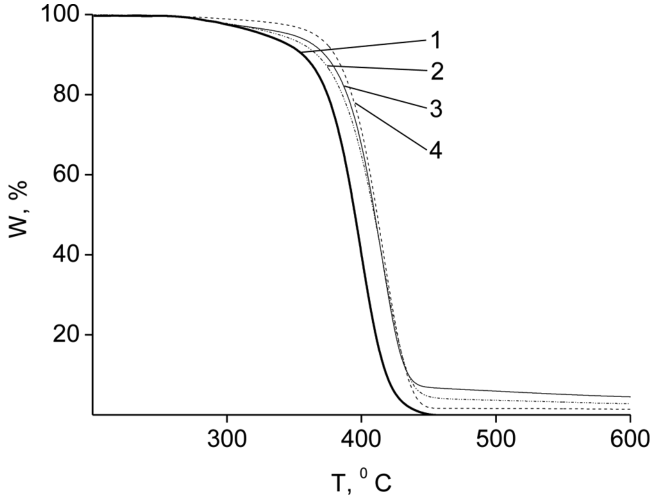


Figure 1. TG curves for PS (1); PS-p-MAPMA (2); PS-p-ENDPMA (3), and PS-p-MTGFTIPMA (4) at an addition content of 3 mol.%.

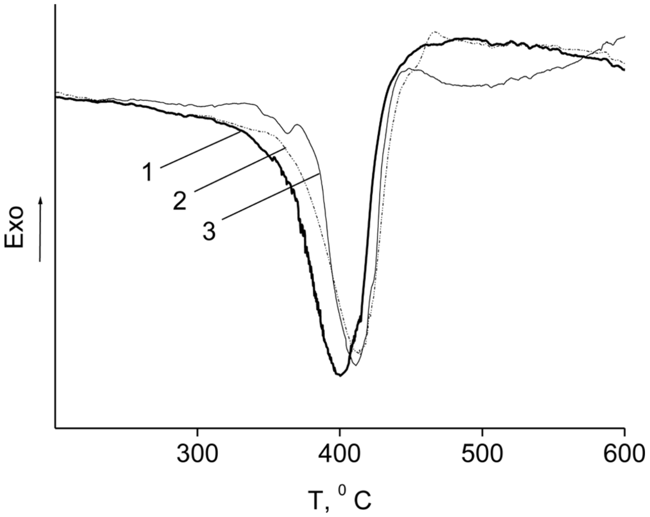


Figure 2. DSC thermal curves for PS (1); PS-p-MAPMA (2), and PS-p-ENDPMA (3) at an addition content of 3 mol.%.

1 mol.% practically not influences its inhibiting action. As an example, the weight loss curves for PS containing 1 and 3 mol% of p-ENDPMA are presented in Figure 3.

In order to study some aspects of the inhibiting mechanism of PS with succinimidophenylmethacrylate derivatives, the mass spectral analysis of desorbed decomposition products (ionization method – electron impact) has been carried out. The mass spectral data on the PS decomposition are given in Figure 4. The peaks corresponding to m/e 39, 51, 63, 77, 91, and 104 which are observed at the same temperature range indicate the possibility that $C_3H_3^+$, $C_4H_3^+$, $C_5H_3^+$, $C_6H_5^+$(phenyl), $C_7H_7^+$ and $C_6H_5C_2H_3^+$ (styrene) can be released [8]. It is suggested that this results from the PS depolymerization process to form styrene and fragments of its molecule. On the mass spectrum of PS-p-MAPMA, we observe, together with the peaks which indicate the PS depolymerization process, other peaks corresponding to m/e 44, 54, 118 and a more intense peak with another shape than that for PS corresponding to m/e 91. This indicates the possibility that $(\text{-O-C=O})^+$, $C_3H_2O^+$, $C_6H_4NCO^+$, and $C_6H_5N^+$ (phenylnitrene) can be released [8]. The ions with m/e

Table 1. Characteristic temperatures of thermal decomposition of polystyrene containing 3 mol.% of additions

Sample	$T_{5\%}{}^a$, °C	$T_{10\%}{}^b$, °C	$T_{40\%}{}^c$, °C	$T_{\max}{}^d$, °C
PS	327	356	390	400
PS-p-MAPMA	338	366	403	414
PS-p-ENDPMA	347	372	404	414
PS-p-MTGFTIPMA	365	380	406	416

[a] Temperature of 5% of weight loss.
[b] Temperature of 10% of weight loss.
[c] Temperature of 40% of weight loss.
[d] Temperature of the maximum rate of weight loss.

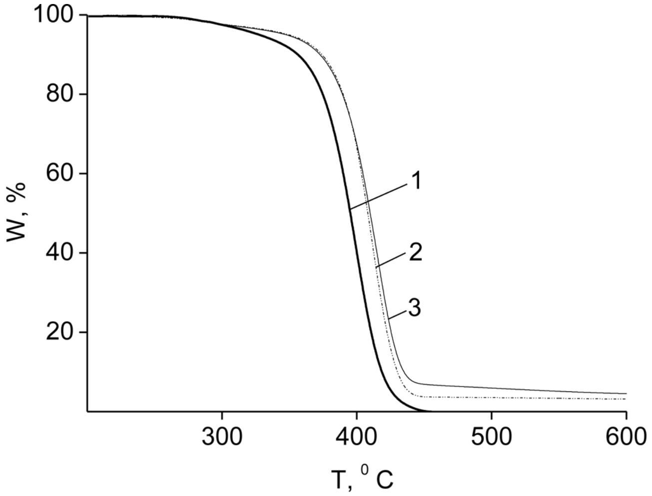


Figure 3. TG curves for PS (1) and PS-p-ENDPMA at addition contents of 1 (2) and 3 mol.% (3).

44, 54, 91, and 118 can appear due to the decarboxylation and the decomposition of phenylmaleimide units. The decarbonylation of phenylisocyanate $C_6H_4NCO^+$ can produce phenylnitrene ion $C_6H_5N^+$ with m/e 91 which is enough active and can react with all kinds of free radicals [9]. The mass spectrum of PS-p-ENDPMA together with peaks observed on the same for PS-p-MAPMA testifies to the presence of the peak with m/e 66 which indicates the possibility that $C_5H_6^+$ (cyclopentadiene) is released (Fig. 5). It is suggested that, during the heating of PS-p-ENDPMA, the retro-Diels–Alder reaction occurs and produces diene - cyclopentadiene and dienophile containing maleimide cycle which is decomposed then, as PS contains p-MAPMA units. For PS-p-MTGFTIPMA, the corresponding diene

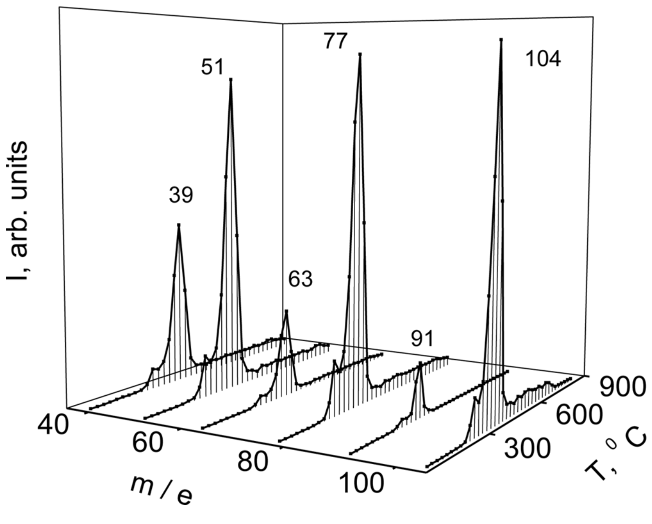


Figure 4. Mass spectrum data for PS decomposition.

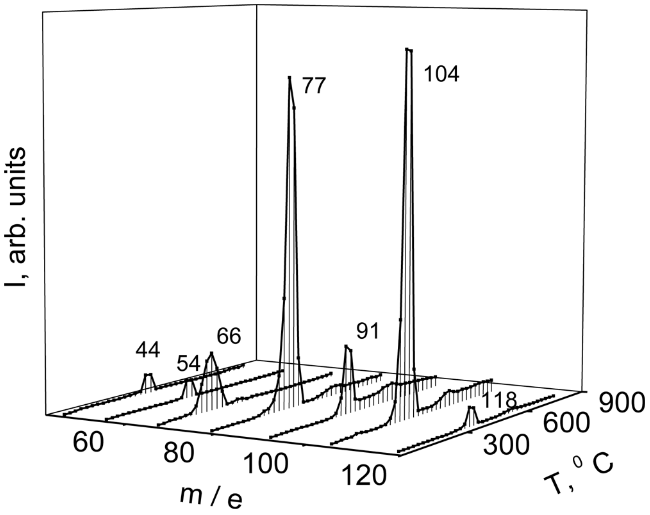


Figure 5. Mass spectrum data for PS-p-ENDPMA decomposition at an addition content of 3 mol.%.

$C_5H_8^+$(2-methylbutadiene-1,3) with m/e 68 is also released together with fragments CH_3^+ and $C_2H_3^+$ with m/e 15 and 27, respectively. The release of diene and its fragments during the heating of PS-p-MTGFTIPMA occurs at a higher temperature than that, at which addition-free PS starts to decompose. The former was registered to be 85 degrees higher than that for the release of cyclopentadiene.

It has been widely accepted that the basic feature of the PS decomposition in the inert atmosphere involves a radical chain process [10]. Phenylnitrene ions formed during the decomposition of a phenylmaleimide unit which is contained in all applied additions react with macroradicals and thus have some inhibiting influence on the PS decomposition. Dienes formed during the decomposition of molecular units containing succinimidophenylmethacrylate derivatives apparently also react with macroradicals, which gives the additional inhibiting influence upon the PS decomposition. It is evident that PS-p-ENDPMA and PS-p-MTGFTIPMA are more thermally stable than PS-p-MAPMA. The most effective inhibitor among succinimidophenylmethacrylate derivatives turns out more thermally stable than addition-free PS, in particular, p-MTGFTIPMA.

Conclusions

All the studied succinimidophenylmethacrylate derivatives prepared by the Diels–Alder reaction reveal the inhibiting effect on the thermal decomposition of polystyrene in the argon atmosphere. The inhibition effectiveness of an addition is determined by the thermal stability of succinimidophenylmethacrylate derivative comparing with addition-free polysterene and does not practically depend on its content in the investigated concentration range. The products of the decomposition of phenylmaleimide units have some inhibiting influence upon the PS decomposition. Dienes formed during the decomposition of molecular units containing succinimidophenylmethacrylate derivatives give an additional inhibiting influence upon the PS decomposition.

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