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Thermomechanical properties and chemical resistance of alkyl methacrylate/*N*-(4-chlorophenyl)maleimide copolymers

Summary — The copolymerizations of methyl, ethyl, butyl, pentyl, or octyl methacrylates with *N*-(4-chlorophenyl)maleimide [*N*-(4-ClPh)MI] initiated with benzoyl peroxide at the temperature range 60—110°C were carried out. The content of *N*-(4-ClPh)MI in the initial mixtures of the monomers were 5 or 10 wt. %. *N*-(4-ClPh)MI was synthesized from maleic anhydride and 4-chloroaniline, in a two-step reaction. Selected properties of resulting copolymers, *e.g.* thermal stability, chemical resistance, Vicat softening point, T_g and hardness were determined. The influences of *N*-(4-ClPh)MI content in the copolymers and the length of alkyl group in methacrylates on their properties were discussed.

Key words: copolymers, alkyl methacrylates, *N*-(4-chlorophenyl)maleimide, thermal stability, chemical resistance, glass transition temperature, hardness.

Polymethacrylates show rather poor thermal stability and some their other properties, *e.g.* hardness, softening point, chemical resistance, are also not fully satisfactory [1—4]. The use of maleimides in the copolymerization with alkyl methacrylates gives the possibility to synthesize the copolymers with higher thermal strength and in addition, the copolymers containing units of *N*-(monohalogenphenyl)maleimide are also less flammable. Many publications appeared describing the chemical modification of various vinyl polymers (such as polymers of: styrene, alkyl acrylates or methacrylates, vinyl acetate, vinyl chloride, vinylidene chloride, and also butadiene) by an addition of *N*-substituted maleimides (*N*-aryl- or *N*-alkyl-aryl-) as well as *N*-(monohalogenphenyl)maleimides [5—19]. In earlier papers we described some properties and reactivity ratios of alkyl(meth)acrylates (methyl, ethyl, butyl) and also styrene with *N*-phenyl- and *N*-tolylmaleimides [15, 16] as well as some properties, and UV ageing study of the copolymers of chosen alkyl methacrylates with N-(monohalogenphenyl)maleimides [17—19].

In this paper the further studies on the synthesis of *N*-(4-chlorophenyl)maleimide [*N*-(4-ClPh)MI] and preparation of the copolymers with methyl, ethyl, butyl, pentyl and octyl methacrylates are reported. The copolymers differing in compositions were obtained by free radical bulk polymerization. The studies were undertaken in order to obtain information concerning the effects of the content of *N*-(4-ClPh)MI and the length of alkyl group in methacrylates on thermal strength, chemical resistance, glass transition temperature (T_g) and hardness of respective copolymers. The copolymers were expected to show better physico-chemical properties than homopolymers of methacrylates.

EXPERIMENTAL PART

Materials

— Methyl methacrylate (MMA), pure (Chemical Works, Oświęcim, Poland), n_D^{20} = 1.4145, d_4^{20} = 0.9424 g · cm^{-3}.

— Ethyl methacrylate (EMA), pure (A.G. Fluka, Switzerland), n_D^{20} = 1.4140, d_4^{20} = 0.9110 g · cm^{-3}.

— Butyl methacrylate (BMA), pure (Chemical Works, Oświęcim, Poland), n_D^{20} = 1.4210, d_4^{20} = 0.8940 g · cm^{-3}.

MMA, EMA and BMA were separated from the inhibitor using the standard manner [20], dried over anhydrous magnesium sulphate, and then distilled under reduced pressure just before use.

— Pentyl and octyl methacrylates (PMA and OMA, respectively) were prepared by transesterification from MMA and corresponding alcohols, as described elsewhere [21—23]. PMA: n_D^{20} = 1.4217, d_4^{20} = 0.8913 g · cm^{-3}; OMA: n_D^{20} = 1.4378, d_4^{20} = 0.8830 g · cm^{-3}.

— Benzoyl peroxide (BP), pure grade (Argon, Łódź, Poland), contained 86.5% BP as determined by iodometric titration [20].

— Laboratory grade reagents as well as organic solvents, inorganic acids and alkalies were used: maleic anhydride, 4-chloroaniline, sodium acetate, ethanol, acetic anhydride, acetone, benzene, ethyl acetate, 1,4-dioxane, chloroform, acetic acid, hydrochloric acid aq., nitric acid, sulphuric acid (concentrated or diluted aq. sol.) and sodium hydroxide (10%, 40% aq. sol.).

Synthesis *N*-(4-ClPh)MI

A solution of maleic anhydride (19.6 g, 0.2 mol in 75 mL of acetone) was added to a solution of 4-chloroaniline (25.5 g, 0.2 mol in 75 mL of acetone) and the mixture was stirred at room temperature for 1.5 h. The yellow precipitate *i.e.* *N*-(4-chlorophenyl)maleamide was filtered off and dried. Yield of this maleamide was 90% (40.6 g) the melting temperature (m.p.) 189—191°C. Then, acetic anhydride (75.0 mL) and sodium acetate (7.0 g) were added to 40.6 g (0.15 mol) of *N*-(4-chlorophenyl)maleamide, obtained in the first step of reaction. The solution was stirred at 80—90°C for 1.5 h. On the completion of reaction the mixture was poured into cold water. A yellow precipitate was obtained and recrystalized from ethanol to give needles with 75% yield, m.p. 108—109°C. Elemental analysis of $C_{10}H_6ClNO_2$ (207.62): calc. (%) C — 57.83, H — 2.89, N — 6.75; found (%) C — 59.78, H — 2.88, N — 6.81.

^1H NMR spectrum of *N*-(4-ClPh)MI is shown in Figure 1. The following resonance signals were found: 6.85 ppm (2H, 2a H-C=C-H) and 7.16—7.67 ppm (m 4H, 2b, 2b'-C_6H_4-).

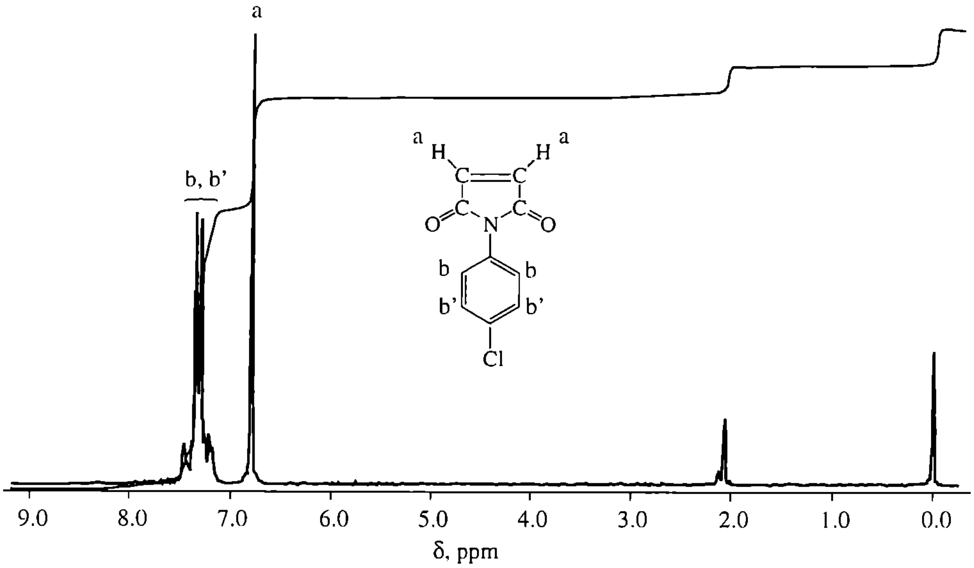


Fig. 1. ^1H NMR spectrum of N-(4-ClPh)MI

IR spectrum had characteristic bands: 1175 cm^{-1} (C=C), 1713 cm^{-1} (C=O), 514 cm^{-1} (C-Cl).

Synthesis of the copolymers and homopolymers

N-(4-ClPh)MI was copolymerized MMA, EMA, BMA, PMA and OMA by free-radical bulk polymerization using 0.3 wt. % of BP as initiator. The content of *N*-(4-ClPh)MI in the initial mixture of comonomers was about 5.0 or 10.0 wt. %. Under the same conditions the homopolymers of methacrylates were obtained. The bulk polymerization was carried out in glass ampules, which were heated in a water thermostat and held at various temperatures and times (at 60°C for 24 h, at 70°C for 24 h, and at 80°C for 22 h). Then the ampules were transferred to the thermostat, and the heating was continued: at 90°C for 23 h, at 100°C for 24 h, and at 110°C for 20 h, respectively. Next the products were cooling down with a rate 5 deg/h.

Methods

— IR spectra of KBr pallets were taken using "Paragon 1000" FT-IR spectrometer (Perkin-Elmer, Beaconsfield, England).

— Elemental analyses were carried out using EA1108 elemental analyzer (Carbo Erba, Milan, Italy).

— Thermal studies were carried out for the powdered samples using OD-102 derivatograph (Budapest, Hungary). The measurements were made at the temperature range 20—1000°C with heating rate of 10°C · min^{-1} in an inert atmosphere (argon), for samples weighed 20—50 mg. The sensitivity of DTA was 1/20 and sensitivity of DTG 1/10. Thermal studies were also carried out with static Madorsky's method [24] for the homo- and copolymers in an oxidizing atmosphere (air) at the temperature range 100—350°C or 100—400°C for some samples, with sample weights of 20—50 mg.

— The Vicat softening temperature ($T_{m,v}$) was measured in a Vicat test using Rσ Caest-Torino apparatus (Torino, Italy). The measurements were carried out for the samples in a form of disks (diameter *ca.* 30 mm, thickness *ca.* 5 mm) with a load of 49 N at heating rate of 50 deg · h^{-1}.

— T_g was estimated using Höppler consistometer (VEB Prüfgeräte-Werk, type 0481, Medingen, Germany). The load was 0.5 kg.

— The hardness (H_k) was measured using a Brinell tester (HPK, Feinmechanic, Ralf Kögel, Engelsdorf, Germany). The samples were in the form of disks (diameter *ca.* 30 mm, thickness *ca.* 5 mm). Hardness was calculated from the formula:

$$H_k = F / d \pi h \qquad (1)$$

where: F — *load*, d — *diameter of the probe ball*, h — *depth of cavity*.

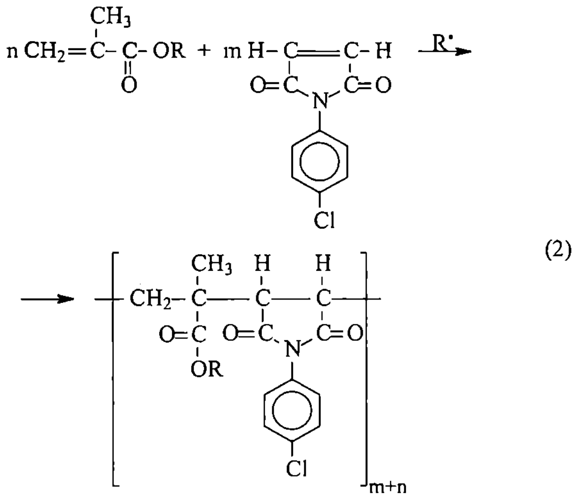
— Chemical resistance of the samples was examined according to the standard procedure required by Polish Standard [25]. The copolymer sample was immersed in an aggressive medium for 7 days. The following organic solvents, inorganic acids and bases were used: acetone, benzene, ethyl acetate, 1,4-dioxane, chloroform, acetic acid, hydrochloric acid aq., nitric acid, sulphuric acid (concentrated or diluted aq. sol.), and sodium hydroxide (10% and 40% aq. sol.). The changes in samples appearances were recorded.

All the previous measurements were made for the homo- and copolymers, which contained 5 or 10 wt. % of maleimide.

^{1}H NMR ($CDCl_3$ solution) spectra of *N*-(4-ClPh)MI (recorded in δ units) were obtained using BS 587A Tesla spectrometer (Brno, Czech Republic) at a frequency of 80 MHz.

RESULTS AND DISCUSSION

The simplified reaction scheme of the copolymerization is the following:



(2)

where: R = $-CH_3$, $-C_2H_5$, $-C_4H_9$, $-C_5H_{11}$, $-C_8H_{17}$.

We stated, that the polymerization were carried out sufficiently long and at such temperature regime, that practically all the comonomers had converted into polymer. It was checked by elemental and IR analyses. The homo- and copolymers were solid, light-yellow, hard (MMA, EMA) or soft (BMA, PMA, OMA) transparent resins. The compositions of the obtained homo- and copolymers and the results of elemental analyses are shown in Table 1. The IR spectrum of EMA/*N*-(4-ClPh)MI copolymer as an example is shown in Fig. 2. Following bands in the ranges: 2980—2950 cm^{-1} (corresponding with ArH groups), 1750—1730 cm^{-1} (for the groups C=O), 1280—1160 cm^{-1} and 1100—1000 cm^{-1} (for the esters groups), 1494—1465 cm^{-1} (for ArH), 1171—1143 cm^{-1} (for the groups $-C \equiv N$) and 810—750 cm^{-1} (for ArCl) were observed. All spectra are characterized by the intense absorption bands of methacrylates and of

Table 1. Compositions and the results of elemental analysis of the homo- and copolymers of alkyl methacrylates with *N*-(4-ClPh)MI

Alkyl methacrylate	Sample No	Composition of initial mixture of comonomers		Elemental analysis, wt. %					
		Alkyl MA	*N*-(4-ClPh)MI	calculated			found*)		
				N	C	H	N	C	H
MMA	1	100	–	–	–	–	–	–	–
	2	95	5	0.34	59.89	7.75	0.58	61.81	8.64
	3	90	10	0.68	59.78	7.49	0.86	59.88	7.45
EMA	4	100	–	–	–	–	–	–	–
	5	95	5	0.34	62.74	8.47	1.16	64.36	8.71
	6	90	10	0.68	62.62	8.18	1.32	64.04	8.48
BMA	7	100	–	–	–	–	–	–	–
	8	95	5	0.34	67.12	9.51	1.56	68.17	9.43
	9	90	10	0.68	66.63	9.16	1.63	68.20	9.32
PMA	10	100	–	–	–	–	–	–	–
	11	95	5	0.34	68.66	9.89	0.61	68.86	11.44
	12	90	10	0.68	68.09	9.52	0.78	56.18	8.22
OMA	13	100	–	–	–	–	–	–	–
	14	95	5	0.34	71.98	10.69	0.67	73.04	12.26
	15	90	10	0.68	71.24	10.29	1.07	72.56	11.77

*) Average values from two independent determinations.

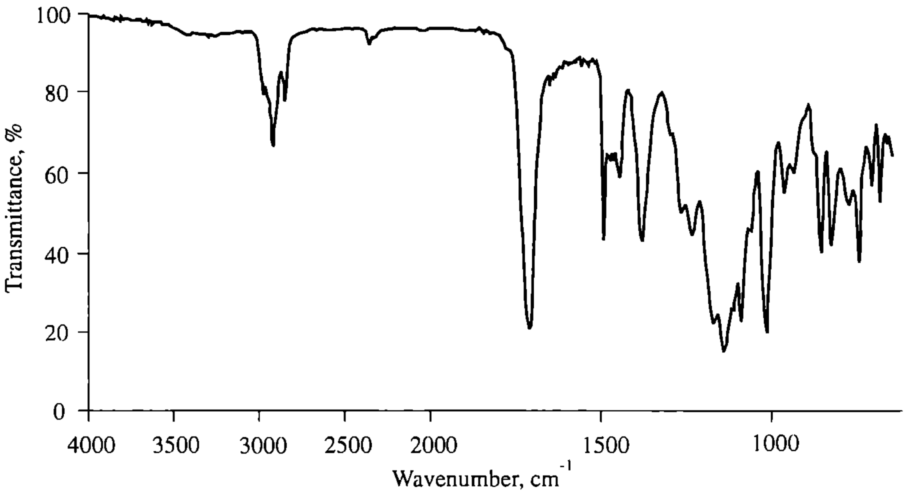


Fig. 2. IR spectrum of sample 6 (in Table 1)

maleimides. No absorption band for unreacted C=C double bond in the range 1640 to 1660 cm^{-1} was observed.

Thermal stability of homo- and copolymers was characterized by three parameters: the temperature of initial (5%) weight loss of the sample (T_{di}), the temperature of 50% weight loss of the sample (T_{d50}) and the temperature of the maximum decomposition rate *i.e.* the appearance of maxima on the DTG curves (T_{max}). The results are presented in Table 2. Figure 3 shows the typical TG, DTG and DTA curves for sample 6 in Table 1.

Table 2. Values of T_{di}, T_{d50} and T_{max} of homo- and copolymers, determined by a dynamic method in argon atmosphere. T^*_{d50} means T_{d50} value determined by the static method in air

Sample No according to Table 1	T_{di}, °C	T_{d50}, °C	T_{max}, °C	T^*_{d50}, °C
1	220	310	330	320
2	240	340	360	355
3	260	370	390	380
4	205	280	273	300
5	210	339	342	330
6	212	358	360	350
7	195	245	260	260
8	220	310	352	335
9	238	340	360	345
10	195	290	320	300
11	205	325	340	330
12	220	330	370	360
13	210	300	320	265
14	215	330	335	320
15	230	340	355	350

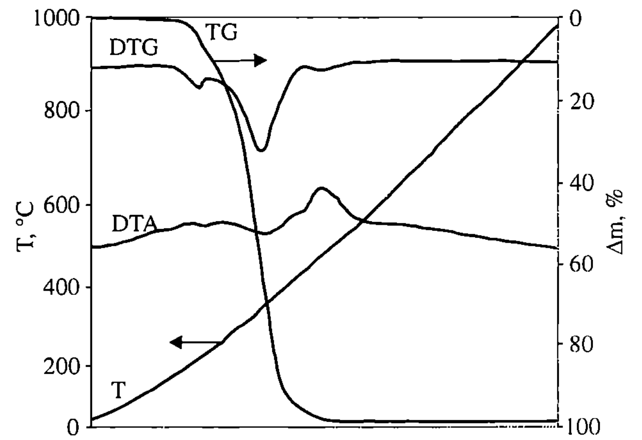


Fig. 3. Thermogram of sample 6 (in Table 1) determined in argon atmosphere

As expected, the highest weight loss *i.e.* lowest values of T_{di} and T_{d50} were observed for homopolymers. The values T_{max} and T_{d50} are shifted toward the higher temperature region with increase in *N*-(4-ClPh)MI content. Thermal effects occurring while heating the sample are observed on DTA curves. The endothermal processes of depolymerization and evaporation occurred at about 360—370°C after above 75% weight loss of the sample (Fig. 3).

Thermal studies of the copolymers have been also conducted by static (Madorsky's) method [24]. Two series of measurements were carried out for the homo- and copolymers containing *ca.* 5 or 10 wt. % of imide. Thermal stability of the homo- and copolymers was indicated as the temperature of 50% weight loss of the sample (T^*_{d50}). T^*_{d50} data concerning homo- and copolymers are shown in Table 2. There is also clear here that the values of weight loss varied considerably dependently on the copolymer composition and the direction of these changes is similar as in the case of T_{d50} values, determined by dynamic method. Analyzing T_{d50} and T^*_{d50} values obtained by dynamic and static methods, respectively, we can state, that such results confirm the thermal stabilizing influence of imide monomer units on the copolymer strength. Already 5 wt. % of imide in the copolymers caused a rise of discussed values from about

30 to about 75 deg, measured both by dynamic and static methods. The length of alkyl group in methacrylates exerts a certain effect on the thermal stability of homo- and copolymers. The values T_{di}, T_{d50}, and T_{max} in general slightly decreased when the length of alkyl group in the methacrylates increased (Table 2).

Thermal stabilities of the copolymers were also examined by Vicat softening point measuring. The data in Table 3 show that among the copolymers of given kind the differences are rather small, while $T_{m,v}$ values of the copolymers are significantly shifted towards the lower temperature the longer is the alkyl chain, exactly as it is known for the methacrylate homopolymers [1, 2]. Instead, in all cases independently on the length of an alkyl chain, an increase in $T_{m,v}$ value occurs. Just the presence of 5 wt. % of N-(4-ClPh)MI affects significantly, in general. This also confirms the thermal stabilizing effect of N-(4-ClPh)MI.

Table 3. Some physical properties of homo- and copolymers of alkyl methacrylates with N-(4-ClPh)MI

Sample No according to Table 1	T_g, °C	H_k, 10^4 N/m^2	$T_{m,v}$, °C
1	104	900	107
2	108	912	110
3	112	1149	113
4	65	1190	67
5	87	1368	83
6	90	2160	86
7	32	600	32
8	40	680	48
9	45	766	52
10	30	*)	28
11	35	*)	32
12	39	*)	41

*) Sample too rubbery for testing.

Table 3 lists also T_g and H_k values of the homo- and copolymers. The same patterns of the dependences of these parameters on N-(4-ClPh)MI content and the length of an alkyl chain in methacrylates were observed as for $T_{m,v}$. Thus, MMA/N-(4-ClPh)MI or EMA/N-(4-ClPh)MI, copolymers show significantly higher hardness than BMA/N-(4-ClPh)MI, while in the case of PMA/N-(4-ClPh)MI samples are just too rubbery for testing.

Studies of chemical resistance (Tables 4 and 5) showed that all homo- and copolymers are soluble or partially soluble in the following organic solvents: acetone, benzene, ethyl acetate, 1,4-dioxane, chloroform, and acetic acid. The samples are resistant against 10% aq. sol. of hydrochloric and nitric acid, 70% aq. sol. of sulphuric acid, and also against 10 and 40% aq. sol. of sodium hydroxide. Concentrated (98%) sulphuric acid causes the decomposition of homo- and copolymers. In 36% aq. sol. hydrochloric acid and in 40% aq. sol. nitric acid they are partially soluble (cloudy systems).

Table 4. Chemical resistance of homo- and copolymers of alkyl methacrylates with N-(4-ClPh)MI against some organic solvents*)

Sample No according to Table 1	Acetone	Benzene	Ethyl acetate	1,4-Dioxane	Chloroform	Acetic Acid
1	±	±	±	±	±	±
2	±	±	±	±	±	±
3	±	±	±	±	±	±
4	±	±	±	±	±	±
5	±	±	±	±	±	±
6	±	±	±	±	±	±
7	±	±	±	±	±	±
8	±	±	±	±	±	s
9	±	±	±	±	±	s
10	s	s	s	s	s	s
11	s	s	s	s	s	s
12	s	s	s	s	s	s
13	z	s	s	s	s	z
14	z	s	s	s	s	z
15	z	s	s	s	s	z

*) — partial solubility, s — swelling of the sample, z — samples essentially unafected (some clouded).

Table 5. Chemical resistance of homo- and copolymers of alkyl methacrylates with N-(4-ClPh)MI against inorganic acid and alkalies*)

Sample No according to Table 1	HCl (10%)	HCl (36%)	H_2SO_4 (70%)	H_2SO_4 (98%)	HNO_3 (10%)	HNO_3 (40%)	NaOH (10%)	NaOH (40%)
1	x	z	x	o	x	z	x	x
2	x	z	x	o	x	z	x	x
3	x	z	x	o	x	z	x	x
4	x	z	x	o	x	z	x	x
5	x	z	x	o	x	z	x	x
6	x	z	x	o	x	z	x	x
7	x	z	x	o	x	z	x	x
8	x	z	x	o	x	z	x	x
9	x	z	x	o	x	z	x	x
10	x	z	x	o	x	z	x	x
11	x	z	x	o	x	z	x	x
12	x	z	x	o	x	z	x	x
13	x	z	x	o	x	z	x	x
14	x	z	x	o	x	z	x	x
15	x	z	x	o	x	z	x	x

*) x — resistant, z — partially soluble, o — solubility with destruction.

CONCLUSIONS

In the free-radical bulk copolymerization of methyl, ethyl, butyl, pentyl and octyl methacrylates with N-(4-ClPh)MI the copolymers differing in composition were obtained. Generally, it has been found that with an increase in *N*-(4-ClPh)MI content, thermal stability increases. This confirms the expected thermal stabilizing influence of maleimides. However, thermal stability slightly decreased with an increasing length of alkyl group in methacrylates. Chemical resistance of the copolymers against inorganic acids and bases was found to be rather less independent on *N*-(4-ClPh)MI content.

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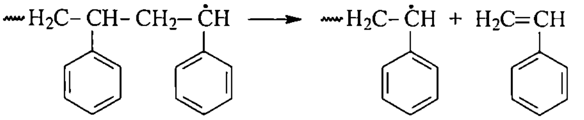
W kolejnym zeszycie ukażą się m.in. następujące artykuły:

- Ciecze elektroreologiczne — materiały, zjawiska, zastosowanie
- Żywice *p*-nonylofenolowo/*o*-krezolowo/cykloheksanowo/formaldehydowe jako modyfikatory kompozycji samoprzylepnych (*j. ang.*)
- Podobieństwo przepływów tworzyw polimerowych w kanałach narzędzi przetwórczych
- Rozkład ciężarów cząsteczkowych w polimeryzacji żyjącej przebiegającej z wymianą segmentów polimerowych spowodowaną przeniesieniem łańcucha na polimer z towarzyszącym rozrywaniem łańcucha. Cz. IV. Układy ulegające cyklizacji (*j. ang*)
- Czy powrotne przeniesienie elektronu wpływa na szybkość fotoinicjowanej polimeryzacji rodnikowej? (*j. ang.*)
- Parametry cząsteczkowe celulozy bakteryjnej. Wpływ temperatury i pH środowiska procesu biosyntezy (*j. ang.*)
- Wpływ chemicznej modyfikacji poli(tereftalanu butylenu) na właściwości elastyczne
- Wpływ grubości próbki i zarodkowania na powierzchniach na kinetykę krystalizacji *i*-PP badaną metodą skaningowej kalorymetrii różnicowej (*j. ang.*)
- Właściwości roztworów oraz powłok prepolimerów polisiloksanouretanowych zawierających mikrożele
- Odwracalna przemiana endotermiczna obserwowana w termoplastycznych elastomerach multiblokowych w przedziale średniej temperatury pomiaru metodą DSC
- Reometryczne badania procesów sieciowania polietylenu i kopolimerów etylenu wobec nadtlenków. Cz. II. Porównanie przebiegu reakcji sieciowania PE-LD, PE-LLD i kopolimeru etylen/octan winylu
- Polimerowo-oligomerowe kompozycje w powłokach lakierowych na przykładzie kompozycji polichlorkowinylowo-epoksydowej

formed lead by β-scission to the formation of various products: new radicals, oligomers and light compounds (*e.g.* toluene, ethylbenzene, cumene, α-methylstyrene).



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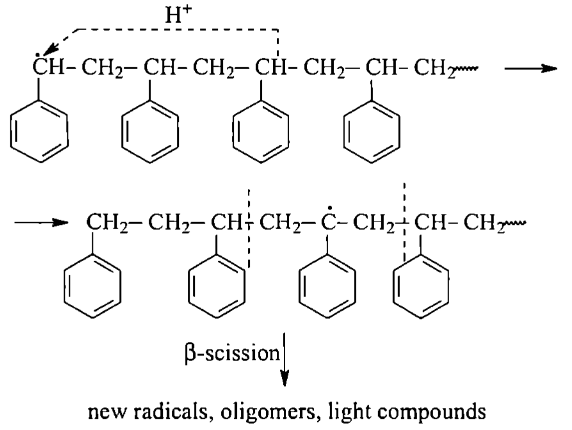

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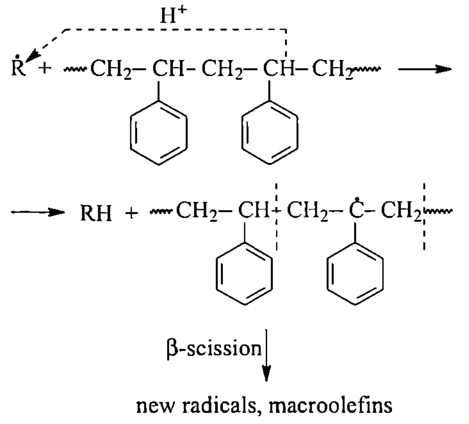
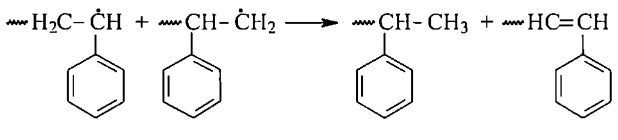


(4)

where:
R — radical reacting with hydrogen of other PS chain
RH = PS



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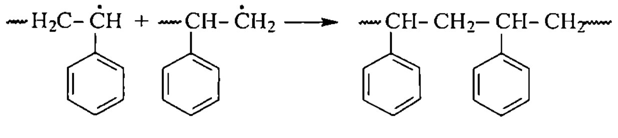

(6)

— Intermolecular transfer — the reaction of the radicals with hydrogen atoms of other chains. This process is analogical to intramolecular transfer and leads to the formation of new radicals and high molecular olefinic compounds.

— Termination — process leading to disappearing of radicals and formation of less-volatile products *via* dismutation and recombination reactions (eq. 5 and 6). During termination, the crosslinking and cyclization reactions often occur.

Much of the papers [10—25] present the studies of PS thermal degradation under processing conditions (200—300°C) or fire. This article reports the results of our studies within the temperature range of 300—600°C under inert or oxidative atmospheres.

EXPERIMENTAL

Materials

The commercial polystyrene (PS) was obtained from Thyssen Schulte (Germany) in the plates form. The density of PS was 1.06 g/cm^3. For the analytical purpose it was ground and the powder obtained was stored in a desiccator.

Degradation of PS

The isothermal degradation of polystyrene was carried out in a flow tubular furnace at temp. of 300°C, 400°C, 500°C, and 600°C, with the reactive gas flow rate 100 cm^3 · min^{-1} and inert gas flow rate 67 cm^3 · min^{-1}. Scheme of the apparatus used for the thermal degradation studies is shown in Fig. 1. The main part of the furnace (1) is a quartz tube (2) consisted of two parts: the outer tube filled always with an inert gas, and the inner tube, where thermal degradation of the analyzed plastic takes place.

A weighed sample of PS (max. 30 mg) was placed in a quartz boat (3) and inserted into the inner tube with a magnet. The less-volatile products evolved during PS thermal degradation were collected on the glass wool (7) and extracted with methanol after the experiment. The gaseous products were collected in the gas sampling pipette (8) in the certain time intervals (after 2, 5, and 10 min) and then analyzed using gas chromatography method.

Methods

Thermogravimetry

The dynamic investigations were performed using the "SHIMADZU TA51" thermogravimetric analyser. The thermogravimetric curves were determined in both nitrogen or air atmosphere with the gas flow rate of 20 cm^3 · min^{-1} and various heating rates (5, 10, and 20°C · min^{-1}). Every time the polymer sample (about 12 mg) was placed as a thin layer in a quartz crucible. The characteristic values of temperature (see Table 1) have been determined using TA 50MW computer programme, which had been developed based on German