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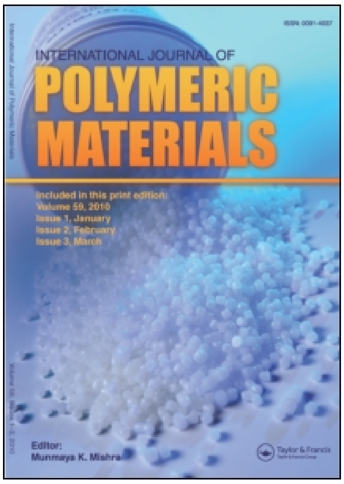

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Copolymerization of Styrene with Bis(4-methacryloylmethylphenyl) Sulphide

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Copolymerization of Styrene with Bis(4-methacryloylmethylphenyl) Sulphide

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A new monomer was prepared in the reaction of bis(4-chloromethylphenyl)sulphide with potassium salt of methacrylic acid. The monomer was characterized by elementary analysis, IR, ^{1}H-NMR and ^{13}C-NMR analyses. After determination of the structure, studies on its solubility with common as well as vinyl solvents such as styrene, methyl methacrylate, butyl acrylate, acrylonitrile, and divinylbenzene were carried out. Besides, a hardening system for styrene solutions of bis(4-methacryloylmethylphenyl)sulphide (BMMPhS) was chosen. Combinations of the following components: benzoyl peroxide, methyl ethyl ketone peroxide, N,N-dimethylaniline, and cobalt naphthenate were used for hardening. Polymerization of the following styrene solutions of BMMPhS: 50, 40, 30, 20 and 10% was performed. The obtained copolymers were tested for mechanical properties like: Young's modulus, tensile strength, elongation at break, hardness of Shore's and Brinnell's methods. For the chosen copolymers, thermal properties were determined.

Keywords: Synthesis of bis(4-methacryloylmethylphenyl)sulphide; (BMMPhS); Unsaturated monomer containing sulphur; Styrene copolymers; Properties of the copolymers

INTRODUCTION

Polystyrene and its copolymers have been prepared on a commercial scale for many years. Most of styrene produced at present is applied for obtaining its copolymers [1]. Papers on improvement of the properties of polystyrene by copolymerization with various monomers of the vinyl type or by copolymerization with butadiene caoutchoucs are numerously presented in chemical literature [2, 3]. Besides, there exists a whole branch of knowledge concerning use of styrene as a curing monomer for unsaturated polyester resins [4–6]. In the Department of Organic Chemistry and Technology, Maria Curie-Skłodowska University in Lublin, studies on the synthesis of monomers and polymers containing sulphur have been conducted for many years [7–9]. One of the obtained results is the methacryloyl derivative of bis(4-chloromethylphenyl)sulphide (BMMPhS). This compound appears to be interesting because it contains sulphur, unsaturated bonds, and ester groups in its chemical structure. As the structure of this compound is similar to that of methyl methacrylate or divinylbenzene that are used for copolymerization with styrene for industrial purposes, we decided to copolymerize it with styrene. It was possible because BMMPhS is well soluble in styrene (1 g/1 cm^3).

Taking the mentioned properties of bis(4-methacryloylmethylphenyl)sulphide into account we determined the influence of its concentration on the properties of styrene solutions. In the experiments BMMPhS was used as a comonomer modifying polystyrene properties.

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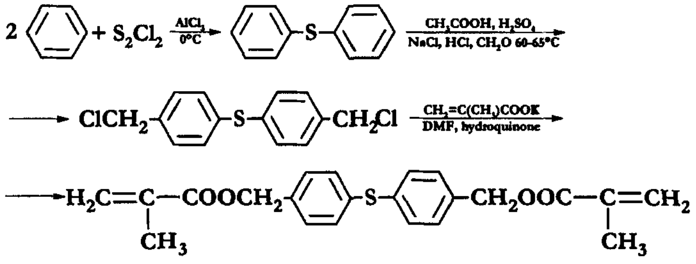
EXPERIMENTAL

Materials

Styrene, cobalt naphthenate (1% Co in styrene) and N,N-dimethylaniline (10% solution in styrene) were from POCh (Gliwice, Poland). Luperox (50% solution of methyl ethyl ketone peroxide in dimethyl phthalate) was from Luperox (Gunzburg, Germany). Benzoyl peroxide (50% paste) came from "Organika-Sarzyna" Chemical Plant (Nowa Sarzyna, Poland).

Bis(4-methacryloylmethylphenyl)sulphide (BMMPhS) was obtained as a result of three step synthesis shown in Scheme 1.

Diphenyl sulphide was obtained as a result of Friedel-Craft reaction of benzene with S_2Cl_2. Purification was made by vacuum distillation at 162–163°C/18 mm Hg. Chloromethylation of diphenyl sulphide was performed by dropping concentrated H_2SO_4 to the mixture of diphenyl sulphide, CH_3COOH, NaCl, HCl and CH_2O. The crude product was recrystallized from methanol [10]. The melting-point of bis(4-chloromethylphenyl)sulphide was 97–98°C. Methacrylic acid



SCHEME 1

potassium salt was obtained by the reaction of KOH with methacrylic acid in the dichloroethane solution [11]. Synthesis of bis(4-chloromethylphenyl)sulphide with methacrylic acid potassium salt was carried out in the DMF solution at its boiling point in the presence of hydroquinone and argon atmosphere [12–14]. The yield of BMMPhS was ca. 41%, and its melting-point after recrystallization from methanol was 42–44°C.

BMMPhS was characterized by elemental analysis (Perkin–Elmer CHN2400), IR (Perkin–Elmer 1725), ^{1}H-NMR and ^{13}C-NMR (BS567 Tesla, Czechoslovakia).

The results of elemental analysis are shown in Table I.

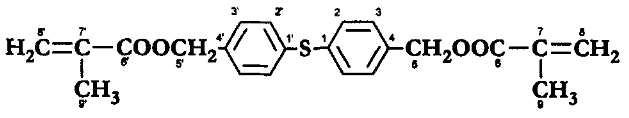
The results of NMR are presented in Table II.

Copolymerization

In order to carry out copolymerization, 40% solution of BMMPhS in styrene was made. The quality of hardening system was defined based

TABLE I Results of elemental analysis

%	*Calculated*	*Found*
C	69.09	69.23
H	5.80	5.80



SCHEME 2

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TABLE II Results of NMR analyses

^{1}*HNMR*		^{13}*CNMR*	
Proton	*Chemical shift (ppm)*	*Carbon*	*Chemical shift (ppm)*
$CH_2=$	6.15; 5.59	1, 1′	136.13
		2, 2′	
CH_3-	1.96	3, 3′	128.75
		4, 4′	135.50
$-CH_2-$	5.17	5, 5′	65.69
		6, 6′	167.01
		7, 7′	131.09
	7.32	8, 8′	128.76
		9, 9′	18.16

The bands are as follows: $C{=}O$ (1713); $=C-H$ (3024); $-CH_3$ (2982); $C{=}C$ (1637); $C-CH_3$ (1381); $C{=}C-COOH$ (961); $C-O$ (1322). IR spectrum doesn't show band CH_2-Cl (1260).

on the gelation time at room temperature. As a hardening system the following combinations were used: benzoyl peroxide (BP) and N,N-dimethylaniline (DMA); and Luperox (L), N,N-dimethylaniline, and cobalt naphthenate (Co). Different hardening systems and gelation times for 40% styrene solution of BMMPhS are summarized in Tables III and IV.

Based on the obtained results two hardening systems were chosen. One hardening system consisted of benzoyl peroxide paste (5% by weight to the quantity of styrene solution) and 6% of 10% solution of N,N-dimethylaniline. The other one consisted of 3% by weight Luperox (50% solution), 4% N,N-dimethylaniline, and 1% of cobalt naphthenate (1% solution). Polymerization of 10, 20, 30, 40 and 50% styrene solutions of BMMPhS was performed by using the hardening system consisting of 5% BP + 6% DMA. Besides, 40 and 50% styrene solutions of BMMPhS were polymerized with the hardening system consisting of L (5%) + DMA (4%) + Co (1%). The gelation times of these compositions are shown in Table V. All polymerizations were performed between two glass panels, which were 2 mm apart.

Mechanical Properties

The obtained foiles of copolymer were heated for 4 h at 80°C. Next, they were cut in stripes. Dimensions of stripes were 180 × 10 × 2 mm. The stripes were exposed to the tests for mechanical properties. The results of these tests are shown in Table VI.

TABLE III Influence of hardening system (DMA, BP) on gelation times

Sample	40% *solution of BMMPhS* (*g*)	*DMA* (*g*)	*BP* (*g*)	*Gelation time* (*min*)
1.1	1.014	0.020	0.02	178
1.2	1.000	0.030	0.02	94
1.3	1.008	0.039	0.02	85
1.4	1.007	0.065	0.02	70
1.5	1.000	0.112	0.02	67
1.6	1.005	0.124	0.02	60
2.1	1.013	0.023	0.03	112
2.2	1.016	0.033	0.03	69
2.3	1.018	0.041	0.03	52
2.4	1.011	0.064	0.03	59
2.5	1.013	0.116	0.03	50
2.6	1.015	0.129	0.03	49
3.1	1.002	0.024	0.04	79
3.2	1.006	0.030	0.04	59
3.3	1.011	0.040	0.04	51
3.4	1.013	0.065	0.04	49
3.5	1.014	0.108	0.04	40
3.6	1.015	0.129	0.04	37
4.1	1.012	0.025	0.05	69
4.2	1.016	0.032	0.05	51
4.3	1.008	0.040	0.05	46
4.4	1.000	0.063	0.05	36
4.5	1.000	0.115	0.05	35
4.6	1.012	0.134	0.05	43

DMA – 10% solution of N,N-dimethylaniline in styrene.
BP – 50% benzoyl peroxide paste.

TABLE IV Influence of hardening system (DMA, L, Co) on gelation times

Sample	40% *solution of BMMPhS* (*g*)	*DMA* (*g*)	*L* (*g*)	*Co* (*g*)	*Gelation time* (*min*)
5.1	1.005	0.040	0.041	0.011	388
5.2	1.004	0.039	0.041	0.020	378
5.3	1.007	0.042	0.043	0.034	399
5.4	1.013	0.042	0.041	0.041	405
6.1	1.010	0.040	0.022	0.011	310
6.2	1.009	0.041	0.031	0.011	286
6.3	1.014	0.043	0.043	0.011	390
6.4	1.018	0.043	0.052	0.010	399
6.5	1.015	0.042	0.060	0.010	401
6.6	1.015	0.043	0.073	0.010	410
7.1	1.016	0.022	0.040	0.010	360
7.2	1.018	0.033	0.046	0.013	355
7.3	1.007	0.040	0.041	0.012	385
7.4	1.016	0.050	0.041	0.011	354
7.5	1.001	0.060	0.043	0.010	349
7.6	1.000	0.072	0.042	0.010	362

DMA – 10% solution of N,N-dimethylaniline.
L – Luperox 50% solution of methyl ethyl ketone peroxide in dimethyl phthalate.
Co – solution of cobalt naphthenate containing 1% Co.

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TABLE V Influence of BMMPhS concentration on gelation times

Concentration of BMMPhS in styrene (%)	*DMA* (%)	*NB* (%)	*Co* (%)	*Gelation time* (*min*)
10	6	5	–	195
20	6	5	–	78
30	6	5	–	65
40	6	5	–	40
50	6	5	–	28
Concentration of BMMPhS in styrene [%]		L (%)		
40	4	3	1	266
50	4	3	1	232

TABLE VI Mechanical properties of the studied foils

Foil % of BMMPhS	*Hardening system*	*Elongation* (%)	*Tensile strength* (*MPa*)	*MY*	*Brinnell's hardness* (*MPa*)	*Shore's hardness* (*MPa*)
10	BP + DMA	4.41	14.45	681.69	36.58	59.3
20	BP + DMA	3.35	36.59	1192.33	99.37	69.7
30	BP + DMA	4.25	53.91	1568.20	111.4	76.3
40	BP + DMA	4.99	52.34	1453.10	119.7	78.3
50	BP + DMA	5.00	55.98	1499.40	132.2	82.5
40	DMA+L + Co	6.5	54.89	1474.60	126.7	83.0
50	DMA + L + Co	5.3	55.71	1489.40	137.0	79.2

Thermogravimetric Analysis

Four foiles were chosen for further studies. Their thermal properties were determined by thermogravimetric analysis. Thermograms were run on a Paulik Erdey MOM derivatograph (Hungary). The thermal data are shown in Table VII.

TABLE VII Thermal properties of the foils

	Initial exothermic effect of	*10% loss of the*	*Mass loss at temperature*				
Foil	*decomposition*	*weight*	200°*C*	250°*C*	300°*C*	350°*C*	400°*C*
40% (NB + DMA)	130	340	2.0	4.0	8.0	12.0	30.0
50% (NB + DMA)	140	380	0.8	2.0	3.0	5.0	16.0
40% (DMA + L + Co)	200	380	0.0	1.0	3.0	6.0	20.0
50% (DMA + L + Co)	190	380	0.0	1.0	3.0	6.5	20.0

RESULTS AND DISCUSSION

In Tables III and IV gelation times for 40% solution BMMPhS in styrene with different hardening systems are shown. Studies on hardening system were carried out in such a way that the quantity of one of the components was constant while the others were changed. The concentration of BP in the hardening system was gradually changed in the range from 2% to 13.4%. From the above given data, we should pay special attention to the system consisting of 5% BP and DMA in the range from 2.5% to 13.4%. The shortest gelation time was obtained for the system containing 5% BP and 11.5% DMA. Similar result was obtained for the system 4% BP and 12.9% DMA. Taking into account that the sample 4.4 was hardened with a much smaller quantity of DMA than the samples 3.6 and 4.5, the system used for the sample 4.4 was taken for the subsequent research. In Table IV gelation the times with application of Luperox (L), N,N-dimethylaniline (DMA). and cobalt naphthenate (Co) are shown. These results indicate that gelation times for these compositions are relatively long. The most effective is the system for the sample 6.2, consisting of DMA 4.1%, Luperox 3.1% and Co 1.1%. In further studies the hardening systems like those for the samples 6.2 and 4.4 were used.

In Table V the gelation times for 10, 20 30, 40 and 50% styrene solutions of BMMPhS with application of the system 4.4 and 40 and 50% solutions with the system 6.2 are presented.

From these results we can conclude that the increase of BMMPhS concentration in the styrene solution shortens the gelation times. We can see insignificant differences in the times of gelation when L, DMA and Co systems were used.

Mechanical properties of the achieved compositions are presented in Table VI. From these data we can see that with an increase of BMMPhS concentration, the Young's modulus and hardness of the samples increase. Tensile strengths also increases significantly, whereas elongation differs insignificantly. Elongation becomes higher in the case of the mixture of L, DMA, and Co as a hardening system.

Thermal characteristics for the foiles containing 40 and 50% of BMMPhS are shown in Table VII. From these data one can notice, that compositions with the hardening system 6.2 (L, DMA and Co)

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indicate higher thermal resistance compared with those of 4.4 (BP and DMA). They differ specially in temperatures of the initial decomposition.

Based on the results from Tables VI and VII we can conclude that the achieved compositions have relatively good thermal and mechanical properties.

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