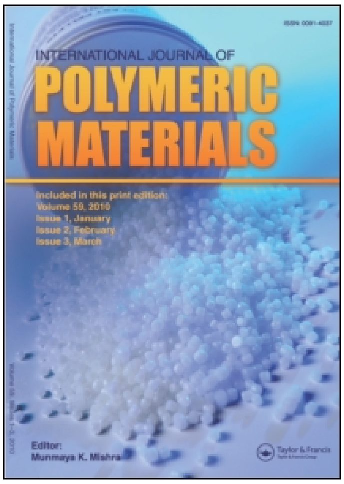

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COPOLYMERIZATION OF BIS(4-METHACRYLOYLMETHYLPHENYL) SULPHONE WITH STYRENE

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Bis(4-methacryloylmethylphenyl)sulphone (BMMPhSu) was prepared by the reaction of bis(4-chloromethylphenyl)sulphone with potassium salt of methacrylic acid. The structure of this new compound was determined by element analysis, IR, ^{1}H-NMR and ^{13}C-NMR analyses. Besides, the fundamental physical properties of bis(4-methacryloylmethylphenyl)sulphone such as the melting point and solubility in common as well as vinyl solvents: styrene, methyl methacrylate, butyl acrylate, acrylonitrile, and divinylbenzene were determined. Using 8 different hardening systems (polymerization initiators) copolymerization of this compound with styrene was carried out. Combinations of the following compounds: benzoyl peroxide, methyl ethyl ketone hydroxyperoxide, N,N-dimethylaniline, cobalt naphthenate, and aromatic amine adduct were used for hardening (polymerization initiation). An influence of BMMPhSu concentration on gelation times with the use of three hardening systems was studied. Finally two hardening systems were chosen and using them copolymerizations of 20 and 25% of BMMPhSu with styrene were carried out. The obtained copolymers were tested for mechanical properties: tensile strength, Young's modulus, elongation at break, hardness by Shore's and Brinnell's methods. Their thermal properties were also determined.

Keywords: Synthesis of bis(4-methacryloylmethylphenyl)sulphone (BMMPhSu); New monomer containing SO_2 group; Styrene copolymers; Properties of the copolymers

1. INTRODUCTION

Polystyrene is one of the most popular polymers. Its commercial production started in 1930 but up till now investigations concerning the improvement of its properties are being carried out [1]. One of the interesting approaches consists of the synthesis of copolymers based on the derivatives of styrene such as chlorostyrene, *p*-methylstyrene or vinylstyrene. Another course is copolymerization of styrene with other vinyl monomers or preparation of

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physical mixtures of polystyrene or its copolymers with butadiene cautchouces or elastomers [2–4]. Additionally, some works concerned with polystyrene manufacturing improvement were carried out. Synthesis and property determination of new styrene copolymers seem to be an important task for science and industry.

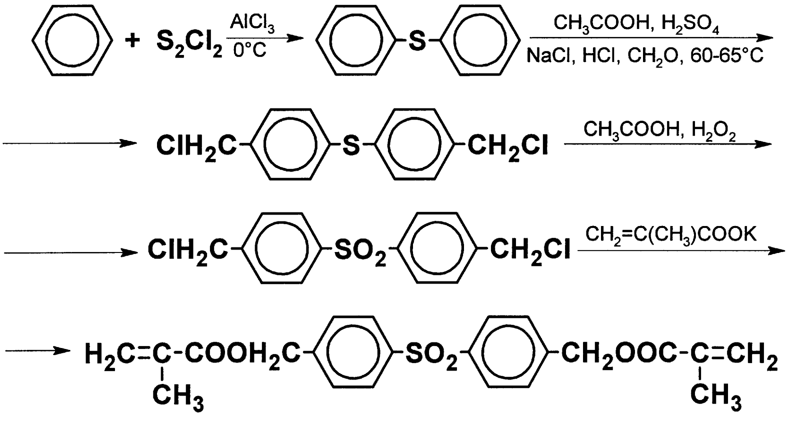
Copolymerization of a vinyl type monomer containing thioether groups with styrene was described in a previous paper [5]. Now, bis(4-methacryloylmethylphenyl)sulphone (BMMPhSu) is presented. This compound contains also unsaturated bonds and sulphur atom in the form of sulphone group. Following the previous studies we copolymerized this compound with styrene and determined the properties of the new copolymers. We also compare some properties of the bis(4-methacryloylmethylphenyl)sulphone – styrene copolymer with those previously described.

2. EXPERIMENTAL

2.1. Materials

Styrene, cobalt naphthenate (1% Co in styrene) and *N*,*N*-dimethylaniline (10% solution in styrene) were from POCh (Gliwice, Poland). Aromatic amine adduct (*p*-toluidine and epoxy resin epidian 5) came from the Department of Polymers, UMCS, Lublin [6]. Luperox (50% solution of methyl ethyl ketone hydroxyperoxide in dimethyl phthalate) was from Luperox (Günzburg, Germany). Benzoyl peroxide (50% paste) came from "Organika-Sarzyna" Chemical Plant (Nowa Sarzyna, Poland). Divinylbenzene and acetonitrile were from Merck while methyl methacrylate from Ventron (Germany). Methanol, ethanol, acetone, benzene, and other solvents were from POCh (Gliwice, Poland).

Bis(4-methacryloylmethylphenyl)sulphone was obtained by the four-step synthesis shown in Scheme 1:



SCHEME 1.

Diphenyl sulphide was obtained as a result of Friedel – Craft reaction of benzene with sulfur chloride. Purification was vacuum distillation at 162 – 163°C/18 mm Hg. Chloromethylation of diphenyl sulphide was achieved by dropping concentrated H_2SO_4 into a mixture of diphenyl sulphide, acetic acid, sodium chloride, concentrated hydrochloric acid, and formaldehyde. The crude product was recrystallized from methanol. The melting point of bis(4-chloromethylphenyl)sulphide was 97 – 98°C.

Bis(4-chloromethylphenyl)sulphone was obtained by oxidation of bis(4-chloromethylphenyl)sulphide with 30% of hydrogen peroxide in concentrated acetic acid. The melting point of the product after recrystallization from ethanol was 146.5 – 147.5°C [7]. Potassium salt of methacrylic acid was obtained by the reaction of potassium hydroxide with methacrylic acid in dichloroethane [8]. The reaction between bis(4-methacryloylmethylphenyl)-sulphone and potassium salt of methacrylic acid was carried out in a solution of dimethyl formamide at the boiling point in the presence of hydroquinone under argon atmosphere [9, 10]. The yield of BMMPhSu was ca. 77.5% and its melting point after recrystallization from methanol was 98 – 100°C.

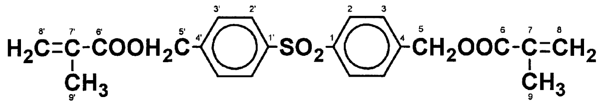
BMMPhSu was characterized by element analysis (Perkin Elmer, CHN 2400), IR (Perkin – Elmer, FTIR-1725), ^{1}H-NMR and ^{13}C-NMR (BS 567 Tesla, Czechoslovakia).

The results of the element analysis are shown in Table 1 while those of NMR in Table 2.

TABLE 1 Results of the element analysis

%	*Calculated*	*Found*
C	63.75	63.68
H	5.35	5.33

TABLE 2 Results of NMR analyses



^{1}*H-NMR*		^{13}*C-NMR*	
Proton	*Chemical shift (ppm)*	*Carbon*	*Chemical shift (ppm)*
CH_2=	6.17; 5.63	1,1′	141.83
		2,2′	128.18
CH_3—	1.96	3,3′	127.84
		4,4′	140.99
—CH_2—	5.23	5,5′	64.91
		6,6′	166.68
	7.99; 7.91; 7.55; 7.46	7,7′	135.69
		8,8′	126.20
		9,9′	18.05

2.1.1. IR (KBr)

The bands are as follows: C=O (1718); =C—H (3089); —CH_3 (2929); C=C (1637); C—CH_3 (1377); C=C—COOH (980); C—O (1299 and 1155). The band CH_2—Cl at 1260 cm^{-1} is not visible in the IR spectrum.

BMMPhSu is nicely soluble in: ethyl acetate, 1,4-dioxane, *N*,*N*-dimethylformamide, styrene (0.3 g/cm^3), methyl methacrylate (0.25 g/cm^3), and acetonitryle (0.6 g/cm^3). Its solubility in methanol, ethanol, acetone, butyl acrylate, and divinylbenzene is rather poor.

2.2. Copolymerization

Copolymerizations were carried out on 25% solution of BMMPhSu in styrene.

As a hardening system (polymerization initiators) the following combinations were used: benzoyl peroxide and *N*,*N*-dimethylaniline (BP + DMA); benzoyl peroxide and aromatic amine adduct (BP + AA); Luperox and cobalt naphthenate (L + Co); benzoyl peroxide and cobalt naphthenate (BP + Co); and BP + DMA + Co; L + DMA + Co; BP + AA + Co; L + AA + Co. To choose the proper hardening system gelation times of this copolymer at room temperature were determined.

2.3. Mechanical Properties

To study the mechanical properties of the copolymers 4 films were prepared. They contained 20 and 25% of BMMPhSu respectively. The mixture of BMMPhSu and styrene with the addition of a proper hardening system was polymerized between two glass panels at room temperature. Next, the films were heated at 80°C for 4 h and cut into stripes of 180 × 10 × 2 mm. The stripes were subjected to tests for mechanical properties. Young modulus, elongation, and tensile strength were measured using TIRA-test 2200, Brinnell's hardness by Kögel, and Shore's hardness by the Zwick apparatus (Germany).

2.4. Thermogravimetric Analysis

Thermogravimetric analysis of the films was carried out using a Paulik–Erdey MOM derivatorgaph (Budapest, Hungary). The obtained data are presented in Table 6.

3. RESULTS AND DISCUSSION

In Table 3 gelation times for 25% solution of BMMPhSu in styrene with different hardening systems are shown. For the hardening system consisting of BP + DMA the concentration of DMA was gradually changed from 1.1

TABLE 3 Influence of the hardening system (DMA, BP, AA, L, and Co) on gelation times

Sample	*25% solution of BMMPhSu* [*g*]	*DMA* [*g*]	*AA* [*g*]	*Co* [*g*]	*BP* [*g*]	*L* [*g*]	*Gelation time* [*min*]
1.1	1.002	0.061	–	–	0.049	–	38
1.2	1.004	0.039	–	–	0.050	–	42
1.3	1.005	0.020	–	–	0.053	–	48
1.4	1.001	0.015	–	–	0.032	–	55
1.5	1.000	0.011	–	–	0.021	–	80
2.1	1.008	–	0.060	–	0.052	–	29
2.2	1.000	–	0.041	–	0.050	–	31
2.3	0.999	–	0.043	–	0.031	–	34
2.4	1.003	–	0.018	–	0.021	–	46
3.1	1.004	–	–	0.032	0.050	–	190
3.2	1.006	–	–	0.015	0.033	–	224
4.1	1.005	–	–	0.040	–	0.040	301
4.2	1.006	–	–	0.018	–	0.031	408
5.1	0.998	0.022	–	0.032	0.052	–	60
5.2	1.004	0.015	–	0.015	0.032	–	66
5.3	0.997	0.012	–	0.005	0.019	–	82
6.1	0.996	0.029	–	0.030	–	0.038	84
6.2	1.001	0.020	–	0.018	–	0.040	130
7.1	0.997	–	0.060	0.031	0.052	–	32
7.2	1.003	–	0.041	0.016	0.033	–	36
7.3	1.004	–	0.019	0.010	0.020	–	49
8.1	1.007	–	0.062	0.031	–	0.040	292
8.2	1.008	–	0.041	0.015	–	0.032	390

to 6.1% while BP from 2.1 to 5.2%. For the hardening system BP + AA the concentration of BP was the same but the concentration of AA changed in the range 1.8–6.0%. Taking into account the shortening of gelation time, homogeneity, and the small shrinkage of copolymers, the system containing aromatic amine adduct (BP + AA) is most effective. The data for the systems L + Co and BP + Co are also presented in this table. The results suggest that those containing Co are less effective and give rather long gelation times. When Co is added to the two component hardening systems (BP + DMA, BP + AA) insignificant prolongation of gelation times is observed. It means that cobalt naphthenate does not accelerate this reaction. Of the three component hardening systems, the system AA + Co + BP caused gelation in the shortest time while the systems AA + Co + L and DMA + Co + L gave rather long gelation times. Both contained Luperox but the latter is more effective.

The obtained results led us to use only three hardening systems in the subsequent studies. They were: I = BP + AA; II = AA + Co + BP; III =

TABLE 4 Influence of the BMMPhSu concentration on gelation time with the use of three hardening systems (I = BP+AA; II = BP+AA+Co; III = L+DMA+Co)

Hardening system	*Concentration of BMMPhSu in styrene* [%]	*DMA* [*g*]	*AA* [*g*]	*Co* [*g*]	*BP* [*g*]	*L* [*g*]	*Gelation time* [*min*]
I	25	–	0.043	–	0.031	–	34
II	25	–	0.042	0.011	0.032	–	36
III	25	0.030	–	0.030	–	0.038	84
I	20	–	0.043	–	0.030	–	58
II	20	–	0.040	0.010	0.031	–	61
III	20	0.033	–	0.031	–	0.043	150
I	15	–	0.041	–	0.030	–	83
II	15	–	0.041	0.010	0.029	–	93
III	15	0.031	–	0.032	–	0.040	198
I	10	–	0.040	–	0.030	–	160
II	10	–	0.040	0.012	0.030	–	171
III	10	0.032	–	0.030	–	0.043	400
I	5	–	0.041	–	0.030	–	340
II	5	–	0.040	0.016	0.030	–	360
III	5	0.030	–	0.029	–	0.042	2040

DMA + Co + L. In Table 4 an influence of BMMPhSu concentration on gelation times of BMMPhSu – styrene copolymers is presented. From these data one can see that independently of the hardening system a decrease of BMMPhSu concentration caused prolongation of the copolymers gelation times.

In Table 5 the mechanical properties of the studied films are gathered. The films were obtained in the presence of two hardening systems I and III. The results indicate that the films obtained by the use of the hardening system containing Luperox are characterized by higher tensile strength and smaller elongation. Also hardness is lower. This phenomenon is especially visible for the data obtained by the Brinnell's method.

TABLE 5 Mechanical properties of the films obtained with the use of hardening systems I and III

Hardening system	*Concentration of BMMPhSu in styrene* [%]	*Elongation* [%]	*Tensile strength* [*MPa*]	*Young modulus* [*MPa*]	*Brinnell's hardness* [*MPa*]	*Shore's hardness* [*MPa*]
I	25	4.9	48.50	1129.3	161.8	85.5
	20	4.8	48.24	1484.9	153.0	82.0
III	25	4.3	52.04	1532.4	123.8	80.5
	20	4.1	51.13	1626.9	147.1	80.0

TABLE 6 Thermal properties of the obtained films

Hardening	*Concentration of BMMPhSu*	*Initial decomposition*	10% *loss of*	*Mass loss at temperature* [%]				
system	*in styrene* [%]	*temp.* [°*C*]	*the weight*	200	250	300	350	400 [°*C*]
I	25	130	360	1.8	3.0	5.0	8.0	24.0
	20	140	350	1.5	3.0	4.5	10.0	25.0
III	25	180	380	0.0	1.0	3.0	7.0	15.0
	20	180	380	0.8	1.0	4.0	7.0	16.0

Thermal properties of the films containing 25 and 20% BMMPhSu are very similar (Tab. 6). Initial decomposition temperatures depend on the character of hardening system used. Higher thermal stabilities are associated with films obtained in the presence of the hardening system containing Luperox.

These results are similar to those for copolymer of bis(4-methacryloylmethylphenyl)sulphide and styrene but with twice smaller concentrations of BMMPhSu [5]. Generally, the new copolymers are harder than those previously studied.

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