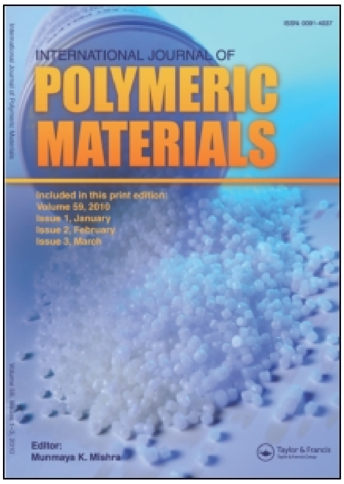

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Copolymerization of methyl methacrylate with bis(4-methacryloylmethylphenyl) sulfide

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COPOLYMERIZATION OF METHYL METHACRYLATE WITH BIS(4-METHACRYLOYLMETHYLPHENYL) SULFIDE

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Bis(4-methacryloylmethylphenyl)-sulfide (BMMPhS) containing sulfur and unsaturated carbon bonds in its structure was used in obtaining copolymers with methyl methacrylate. Copolymerization of the BMMPhS with fixed concentration of methyl methacrylate was carried out in presence of three curing systems:

I BP + DMA
II L + DMA + Co
III (BP + L) + DMA + Co
Where: BP-benzoyl peroxide
DMA-N,N-dimethylaniline
Co-cobalt naphthenate
L-methylethyl ketone peroxide.

In individual experiments the quantitative composition of curing systems was changed and its influence on the gelation time of the copolymers was determined. Besides, the effect of the BMMPhS concentration on the copolymer gelation time was determined. In that case curing system I with stable concentration of its components was used.

For five copolymers the peak exotherm temperatures were determined. These copolymers were formed from 40% solution of BMMPhS using various compositions of curing system I.

Separately, three films were made by polymerization of 60, 40 and 20% solutions of BMMPhS with curing system I, one by polymerization of 40% solution with curing system II, and another one by polymerization of 40% solution with curing system II. The obtained films were tested for mechanical properties such as Young's modulus, tensile strength, elongation at break, hardness of Shore's and Brinnell's methods as well as their thermal properties and glass transition temperatures.

Keywords: unsaturated monomer, bis(4-methacryloylmethylphenyl)-sulfide (BMMPhS), methyl methacrylate copolymers, properties of the copolymers

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INTRODUCTION

A great number of copolymers of methyl methacrylate are described in the literature as this monomer copolymerizes readily with other vinyl compounds. Some of them have found commercial application in various technological branches: electronics, optical electronics, optics, corrosion protection as well as in medicine, particularly in dentistry.

Copolymers of methyl methacrylate with styrene are those most frequently described in scientific literature. They have been applied as: protective coating [1–3] impregnant of wood [4], impregnant of paper [5], material for production of optical junction [6].

Copolymers of methyl methacrylate (MM) with styrene are often modified by the addition of other components or monomers. For instance: copolymer modified by the addition of $Ca_3(PO_4)_2$ or $CaCO_3$ is applied in optics [7, 8] with the addition of butadiene or carboxylic acids to manufacture thermal detectors [9, 10], with the addition of acrylonitryle to produce discs for recording sound or pictures [11].

Examples of commercial applications of methyl methacrylate copolymers with other kinds of vinyl monomers are as follows:

- with butadiene caoutchouc in preparation of optical fibers [12, 13],
- with vinyl ethers as a glue in production of safety glass [14],
- with ethyl and butyl methacrylates in dentistry materials [14–16],
- with vinyl and silicon monomers in preparation of contact lenses [15–19],
- with acrylates siloxanes in cosmetic industry [20, 21].

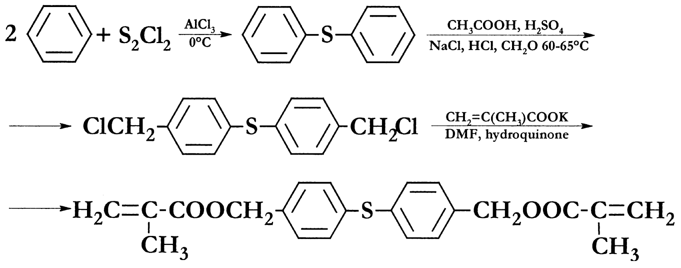
In the Department of Organic Chemistry and Technology, Maria Curie-Skłodowska University in Lublin we obtained bis(4-methacryloylmethylphenyl)-sulfide (BMMPhS) which was described in a previous paper [22] and at present we apply this monomer as a comonomer of methyl methacrylate. The main aim of the experiments described in this article is the determination of the BMMPhS concentration effect on the properties of poly(methylmethacrylate).

EXPERIMENTAL

Materials

Methyl methacrylate (MM) was from Ventron (Germany), cobalt naphthenate(1% Co in styrene) and N,N-dimethylaniline (10% solution in MM) were from POCh (Gliwice, Poland). Luperox (50% solution of methylethyl 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) sulfide (BMMPhS) was obtained in our laboratory as a result of three-step synthesis shown in Scheme 1:



SCHEME 1

Copolymerization

In order to carry out copolymerization, 30% solution of BMMPhS in methyl methacrylate (MM) was prepared (MM was purified from inhibitors). Polymerization of this solution at room temperature was carried out by the use of curing system I consisting of BP (50% benzoyl peroxide paste) and DMA (10% solution of N,N-dimethylaniline in MM).

Concentration of BP and DMA in this curing system changed in the range from 2 to 8% by weight. Efficiency of the curing system was determined based on the gelation time at room temperature. The obtained results are summarized in Table 1.

Next, polymerization of 40% solution of BMMPhS was carried out using curing system II. This curing system consisted of L (luperox 50% solution)+DMA+Co (cobalt naphthenate 1% solution of Co). Concentrations of L and DMA in the curing system were changed from 6 to 10% by weight but concentration of Co was kept at a constant level of 1.5%. Gelation times are shown in Table 2.

The third curing system consisted of the mixture of peroxides (BP+L) (BP and L were used 1 : 1 by weight) and DMA+Co. Gelation times were determined for copolymers containing 40% of BMMPhS. At first the concentrations of (BP+L) and DMA changed but the quantity of Co was stable. Next, concentrations of (BP+L) and DMA were constant (both components 6%) but the concentration of Co changed. The obtained results are shown in Table 3. Besides, polymerization of 60, 50, 40, 30, 20 and 10% solutions of BMMPhS was carried out with use of curing system I. Gelation times of the polymerization are shown in Table 4.

In order to determine peak exotherm temperatures five polymerizations were made (Tab. 5).

Based on the results obtained during determination of curing systems, five films were prepared. Three films were obtained by polymerization of 60, 40 and 20% solutions of BMMPhS using curing system I BP(4%)+

TABLE 1 Influence of the curing system BP+DMA on gelation time

Sample	30% *solution BMMPhS in MM* [*g*]	*BP* [*g*]	*DMA* [*g*]	*Gelation time* [*min*]
1.1	1.003	0.082	0.081	5
1.2	1.001	0.080	0.059	6
1.3	0.998	0.079	0.039	14
1.4	1.002	0.079	0.022	32
2.1	1.004	0.058	0.082	11
2.2	1.001	0.060	0.060	14
2.3	0.999	0.060	0.042	15
2.4	1.004	0.058	0.019	84
3.1	0.998	0.038	0.079	19
3.2	1.003	0.040	0.059	21
3.3	1.000	0.039	0.041	38
3.4	1.003	0.039	0.022	124
4.1	0.997	0.021	0.078	36
4.2	1.002	0.019	0.060	79
4.3	1.001	0.019	0.039	144
4.4	1.001	0.019	0.019	152
5.0*	1.001	0.080	0.080	82

BP – 50% benzoyl peroxide paste.
DMA – 10% solution of N,N-dimethylaniline in MM.
MM – methyl methacrylate.
* Sample without BMMPhS.

TABLE 2 Influence of curing system L+DMA+Co on gelation time

Sample	40% *solution BMMPhS in MM* [*g*]	*L* [*g*]	*DMA* [*g*]	*Co* [*g*]	*Gelation time*
5.1	1.000	0.100	0.099	0.013	149
5.2	1.003	0.082	0.099	0.015	143
5.3	1.002	0.063	0.099	0.016	138
6.1	1.003	0.100	0.079	0.016	194
6.2	1.001	0.081	0.080	0.015	194
6.3	1.002	0.058	0.078	0.014	189
7.1	0.999	0.100	0.059	0.015	315
7.2	1.003	0.082	0.059	0.015	239
7.3	0.999	0.060	0.059	0.016	255

L-luperox (50% solution of methylethyl ketone peroxide).

DMA(6%), one by polymerization of 40% solution with curing system II L(4%)+DMA (6%)+Co(1.5%) and another one by polymerization of 40% solution of BMMPhS with curing system III (BP+L)(4%)+DMA(6%)+Co(1.5%). Polymerizations were performed between two glass panels, which were 2 mm apart. Then, the films were heated for 4 h at 80°C and cut in stripes.

TABLE 3 Influence of curing system (BP + L) + DMA + Co on gelation time

Sample	40% *solution of BMMPhs in MM* [*g*]	*BP + L* 1 : 1 [*g*]	*DMA* [*g*]	*Co* [*g*]	*Gelation time* [*min*]
8.1	1.003	0.079	0.081	0.015	42
8.2	1.002	0.058	0.082	0.015	31
8.3	1.001	0.042	0.078	0.014	38
9.1	0.999	0.080	0.058	0.015	62
9.2	1.001	0.057	0.062	0.015	52
9.3	1.000	0.041	0.058	0.016	46
10.1	1.003	0.079	0.041	0.017	106
10.2	1.001	0.058	0.039	0.015	71
10.3	1.000	0.040	0.041	0.016	54
11.1	1.001	0.060	0.059	0.015	52
11.2	0.998	0.061	0.060	0.030	48
11.3	0.999	0.061	0.059	0.046	49

BP + L-mixture of luperox 50% solution and BP 50% paste (1 : 1 by weight).

TABLE 4 Influence of BMMPhS concentration on gelation time

Concentration of BMMPhS in MM [%]	*BP* [%]	*DMA* [%]	*Gelation time* [*min*]
60	4	6.1	6
50	4	6	8
40	4.1	5.8	13
30	4.3	6.1	20
20	4	6.3	29
10	4	5.7	38

TABLE 5 Peaks exotherm temperature

	40% *solution*	*Curing system*		*Peak exotherm*
Sample	*BMMPhS in MM* [*g*]	*BP* [%]	*DMA* [%]	*temperature* [°*C*]
1	3	8	8	182.5
2	3	8	6	171
3	3	8	4	157.5
4	3	8	2	140
5	3	4	6	144

Mechanical Properties

The dimensions of stripes were 180 × 10 × 2 mm. The stripes were submitted to tests for mechanical properties such as Young's modulus, elongation and

TABLE 6 Mechanical properties of the studied films

Film %conc. of BMMPhS	*Curing system*	*Elongation* [%]	*Tensile strength* [*MPa*]	*MY*	*Brinnell's hardness* [*MPa*]	*Shore's hardness Scale D*
60	BP + DMA	3.7	55.01	1262.1	155.1	83.8
40	BP + DMA	3.5	56.27	1192.3	150.4	82.7
20	BP + DMA	4.8	66.37	1349.3	138.2	82.0
40	L + DMA + Co	3.9	54.6	1728.8	156.8	81.4
40	(BP + L) + DMA + Co	3.2	46.4	1652.9	154.8	82.5

TABLE 7 Thermal properties and temperature of glass transition of the films

	Initial exothermic	*5% loss of*	*10% loss of*	*Mass lost at temp.* [%]				
Film	*effect of decomposition*	*the weight*	*the weight*	200 [°*C*]	250 [°*C*]	300 [°*C*]	350 [°*C*]	T_g [°*C*]
60%(BP + DMA)	260	300	305	0	0	4	30	–*
40%(BP + DMA)	250	295	300	0	0	10	50	145.8
20%(BP + DMA)	220	270	295	1	2	15	56	131.9
40%(L + DMA + Co)	280	310	330	0	0	2	22	135.3
40%([BP + L] + DMA + Co)	280	280	320	1	3	6	25	146.9

T_g-glass transition.
*No T_g in the range from 0°C to 200°C.

tensile strength using the TIRA-test 2200 (Germany), Brinnell's hardness by Koegel (Germany), and Shore's hardness using the Zwick apparatus (Germany) (Results are presented in Tab. 6.)

Thermogravimetric Analysis

Thermogravimetric analysis of the films was carried out using the Paulik-Erdey MOM derivatograph (Budapest, Hungary). The obtained data are presented in Table 7.

Thermal Analysis

Measurements of glass transition temperatures of the films were made using differential scanning calorimeter NETZSCH DSC200 (NETZSCH, Germany). Samples (4 to 17 mg) were heated from 0°C to 200°C at a heating rate 10 K/min. The results are shown in Table 7.

RESULT AND DISCUSSION

In Table 1 gelation times for 30% solution of BMMPhS obtained with the curing system BP + DMA are shown. Experiments were carried out in such a way that one component of the curing system was kept constant and the second one was changed. Next, the second component was maintained constant and the first one was changed. The concentration of BP and DMA in curing system I were changed in the range from 2 to 8% by weight. The data presented in Table 1 show that the gelation times are short for compositions when the curing system including BP from 4 to 8% and DMA from 6 to 8% was used. Gelation times are longer when the curing systems including BP and DMA in the range from 2 to 4% are applied (even if the second component of this system is at high concentration).

It is interesting to note that some gelation times of 30% solution BMMPhS are longer than the gelation time of pure methyl methacrylate in presence of BP(8%) + DMA(8%).

If concentration of BP and DMA in the curing system is low, gelation times are longer than those obtained with curing system II L + DMA + Co and distinctly longer than in the case of curing system III (BP + L) + DMA + Co (see Tabs. 2 and 3).

It also follows from Table 2 that concentration of DMA in the curing system has stronger influence on the gelation time than the concentration of L. The results in Table 3 show that gelation times are generally longer in the case of curing system III compared with system I, but distinctly shorter when system II is used.

The results for samples 11.1, 11.2 and 11.3 show that changes of Co concentration have rather small influence on gelation time of compositions.

It follows from Table 4 that gelation time strongly depends on concentration of BMMPhS in composition when the same curing system is used.

In Table 5 peak exotherm temperatures are presented. It follows from these results that peak exotherm temperatures depend on composition of curing system. For higher concentration of BP and DMA peak exotherm temperatures rise.

Table 6 shows the mechanical properties of the obtained films. From these data one may see that elongation changes in the range 3.2 to 4.8% tensile strength from 46.4 MPa to 66.37 MPa and Young's modulus from 1192.3 to 1728.8. The obtained copolymers are characterized by great hardness reaching 156.8 MPa (Brinnell's method) and 83.7(Shore's method scale D).

In Table 7 the results of thermogravimetric and DSC methods for the studied films are shown. The films are characterized by high initial decomposition temperatures (220 – 280°C) and rather high temperatures of glass transition (131.9 – 146.9°C).

All the obtained films are transparent and very slightly colored except for the film obtained by the use of curing system II, which has insignificant brown tinge.

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