

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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

Wiesław Rudź^a

^a Department of Organic Chemistry and Technology, Maria Curie-Skłodowska University, Lublin, Poland

Online publication date: 27 October 2010

To cite this Article Rudź, Wiesław(2003) 'Copolymerization of methyl methacrylate with bis(4-methacryloylmethylphenyl)-sulphone', *International Journal of Polymeric Materials*, 52: 3, 219 – 228

To link to this Article: DOI: 10.1080/00914030304893

URL: <http://dx.doi.org/10.1080/00914030304893>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

Wiesław Rudź

Department of Organic Chemistry and Technology,
Maria Curie-Skłodowska University, Lublin, Poland

Bis(4-methacryloylmethylphenyl)-sulphone (BMMPHSu), the monomer containing sulphur in the form of sulphone group and two unsaturated bonds C=C in its structure, was applied for obtaining copolymers with methyl methacrylate (MM). 15% solution of BMMPHSu in MM was polymerized in the presence of three curing systems. The curing systems were combinations of benzoyl peroxide (BP), methylethyl ketone peroxide (L), N,N-dimethylaniline (DMA) and cobalt naphthenate (Co). Influence of curing systems on gelation times of the solutions of BMMPHSu in MM at room temperature was determined. The peaks exotherm temperatures were measured. For four polymers containing 15% of BMMPHSu polymerized in the presence of BP and DMA of different concentrations as curing systems. Besides, 8 films of the copolymers BMMPHSu and MM were obtained. The films were obtained by polymerization of 15, 10 and 5% solutions of BMMPHSu using the curing system BP + DMA, and 15% solution of BMMPHSu using the curing systems (BP + L) + DMA + Co and L + DMA + Co. Some of the films (5) were heated for 4 h at 80°C but the others were not. All obtained films were tested for mechanical properties such as Young's modulus, tensile strength, elongation at break, hardness by the Shore's and Brinnell's methods. Thermal resistance and glass transition temperatures of the obtained copolymers were also determined.

Keywords: bis(4-methacryloylmethylphenyl)-sulphone (BMMPHSu), unsaturated monomer containing SO₂ group, methyl methacrylate copolymers, properties of the copolymers

Received 1 December 2000; in final form 5 December 2000.

Address correspondence to Wiesław Rudź, Department of Organic Chemistry and Technology, Maria Curie-Skłodowska University, Gliniana 33, 20-614 Lublin, Poland.

INTRODUCTION

Good mechanical, dielectrical and very good optical properties are characteristic for poly(methylmethacrylate). Its permeability for visible light reaches 92% and for UV light 73%. This characteristic is also revealed by many copolymers of methyl methacrylate, for instance copolymers with styrene [1,2]. Chemical resistance of poly(methylmethacrylate) is not high, because this polymer is soluble in many solvents such as esters, ketones, halogenated hydrocarbons and aromatic hydrocarbons. Copolymers of methyl methacrylate are often modified to improve the following properties: hardness, impact strength, resistance to weather, combustibility, thermal and chemical resistance. Copolymerization or addition of other compounds for changing other properties are rarely used. In this way the following properties are changed: permeability of oxygen by the addition of glycerol methacrylate or by the addition of polyamides and siloxanes [3] or anti electrostatic properties by copolymerization of methyl methacrylate with ionic monomers [4].

For commercial purposes, hardness of materials based on poly(methylmethacrylate) is often controlled by copolymerization or addition of other chemical substances. The typical examples of this kind of polymeric materials are those used in dentistry and for manufacturing contact lenses. To obtain dentistry filling, copolymers of methyl methacrylate and styrene are used [5]. For manufacturing dentures copolymers of methyl methacrylate with ethyl and butyl methacrylates or with fluormethacrylate compounds [6] are applied, whereas for artificial teeth copolymers of methyl methacrylate crosslinked by ethylglycol methacrylate or bis-GMA [7] are used.

Similarly, contact lenses with different flexibility are prepared from copolymers of methyl methacrylate with different vinyl monomers [8]. However, rigid lenses are made using copolymers of methyl methacrylate with tris(trimethylsiloxy) sililpropylene [7].

Materials with increased impact strength are formed by copolymerization of methyl methacrylate with allyl methacrylate [9], with butadiene rubber [10] (optical fiber cores), with natural caoutchoucs [11] (protective covering), with PVC (transparent and opaque sheets applied for instance in cartography) or with N-alkylsulfonated 2-(ethylamino) ethyl methacrylate [12] (photographic materials).

Impact strength, combustibility and chemical resistance of poly(methylmethacrylate) could be increased by the addition of PVC or chlorinated PVC [13,14]. The addition of methylamine to poly(methylmethacrylate) causes a rise in its flexibility [15] (flexible laminates with good thermal resistance).

The resistance to weather increases when methyl methacrylate is copolymerized with chlorinated alkenes or with diene rubbers containing vinyl end groups [16] or when methyl methacrylate is cross-linked by bis maleimides [17] (anticorrosive layers).

The examples mentioned above show only some possibilities of improving the properties of poly(methylmethacrylate).

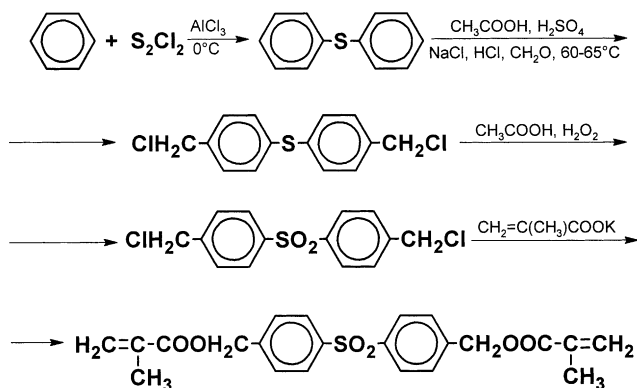
The aim of this paper is to investigate the influence of BMMPHSu and its concentration on properties of copolymers obtained by polymerization with methyl methacrylate.

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)-sulphone (BMMPHSu) [18] was obtained in our laboratory as a result of four-step synthesis shown in Scheme 1:



SCHEME 1

Copolymerization

Before obtaining the copolymers of BMMPHSu and MM, the influence of three curing systems on gelation time of 15% solution BMMPHSu in MM at the room temperature was examined.

The curing systems were as follows:

I BP + DMA, II (BP + L) + DMA + Co, and III L + DMA + Co
where

BP – 50% paste of benzoyl peroxide

L – 50% solution of methylethyl ketone peroxide

DMA – 10% solution of N,N-dimethylaniline

Co – solution of cobalt naphthenate 1% Co by weight.

The concentration of benzoyl peroxide in curing system I was changed in the range 2–8% (by weight) but the concentration of DMA was kept on constant level. Next, the concentration of DMA (from 2 to 8% by weight) was changed but the concentration of BP was constant. The obtained results are given in Table 1.

Curing system II was composed of three components: (a) mixture of benzoyl peroxide and methylethyl ketone peroxide solution which were used in the ratio 1:1 (by weight), (b) N,N-dimethylaniline

TABLE 1 Influence of Curing System BP + DMA on Gelation Times

Sample	15% solution of BMMPHSu in MM [g]	BP [g]	DMA [g]	Gelation time [min]
1.1	0.999	0.079	0.082	13
1.2	1.005	0.079	0.058	10
1.3	0.996	0.079	0.041	10
1.4	1.003	0.081	0.021	14
2.1	0.998	0.060	0.079	13
2.2	1.002	0.059	0.058	14
2.3	1.003	0.060	0.038	14
2.4	0.999	0.061	0.021	18
3.1	1.000	0.040	0.078	11
3.2	1.002	0.040	0.059	14
3.3	1.004	0.041	0.039	15
3.4	1.003	0.042	0.021	22
4.1	0.996	0.020	0.082	19
4.2	0.998	0.021	0.061	25
4.3	1.002	0.019	0.041	34
4.4	1.001	0.022	0.021	40
5.0*	1.001	0.081	0.059	71

BP – 50% paste of benzoyl peroxide.

DMA – 10% solution of N,N-dimethylaniline.

MM – methyl methacrylate.

* – sample without BMMPHSu.

TABLE 2 Influence of Curing System (BP + L) + DMA + Co on Gelation Times

Sample	15% solution of BMMPHSu in MM [g]	BP + L Mixture 1:1 [g]	DMA [g]	Co [g]	Gelation time [min]
5.1	1.000	0.078	0.080	0.016	74
5.2	0.997	0.079	0.058	0.016	117
5.3	1.000	0.081	0.040	0.014	168
6.1	1.000	0.057	0.081	0.016	60
6.2	1.002	0.058	0.058	0.015	84
6.3	0.998	0.059	0.041	0.014	120
7.1	1.002	0.039	0.078	0.015	54
7.2	1.003	0.041	0.059	0.014	70
7.3	0.997	0.039	0.040	0.015	83

Co—cobalt naphthenate (1% Co in styrene).

solution and (c) cobalt naphthenate solution. During the investigations, the concentrations of (BP + L) and DMA were changed in the range from 4 to 8% (by weight) but the concentration of Co solution was kept constant at 1,5%. The results of these experiments are presented in Table 2.

The third curing system consisting of L + DMA + Co was tested as follows: concentrations of L and DMA were changed from 6 to 10% and the concentration of Co was kept constant at 1.5%. The results are shown in Table 3.

Besides, using curing system I BP(4%) + DMA(6%), 20, 15, 10 and 5% solutions of BMMPHSu in MM were polymerized. The obtained gelation times are presented in Table 4.

TABLE 3 Influence of Curing System L + DMA + Co on Gelation Times

Sample	15% solution of BMMPHSu in MM [g]	L [g]	DMA [g]	Co [g]	Gelation time [min]
8.1	1.000	0.098	0.101	0.014	260
8.2	1.002	0.102	0.079	0.015	323
8.3	1.002	0.099	0.060	0.014	402
9.1	1.001	0.081	0.098	0.014	263
9.2	1.003	0.079	0.078	0.015	325
9.3	1.002	0.081	0.059	0.015	438
10.1	1.004	0.061	0.097	0.016	288
10.2	1.002	0.058	0.078	0.015	396
10.3	1.000	0.060	0.060	0.015	470

TABLE 4 Influence of BMMPHSu Concentration on Gelation Times

Sample	Concentration of BMMPHSu in MM [%]	BP [%]	DMA [%]	Gelation time [min]
11.1	20	4	6	8
11.2	15	4	6	13
11.3	10	4	6	17
11.4	5	4	6	25

TABLE 5 Peaks Exotherm Temperature

Sample	15% solution of BMMPHSu in MM [g]	Curing system		Temperature [°C]
		BP [%]	DMA [%]	
12.1	3	4	8	143.5
12.2	3	4	6	142.5
12.3	3	4	4	135
12.4	3	4	2	130

Peak exotherm temperatures of polymerization of 15% solution BMMPHSu in MM by the use of curing system I BP + DMA were also measured. Concentration of BP in the curing system was stable (4%) but the concentration of DMA was changed from 2% to 8%. The results are shown in Table 5.

Taking into account the results associated with curing systems, polymerizations of 15, 10 and 5% solutions of BMMPHSu in MM were carried out using curing system I BP(4%) + DMA(6%). Besides, polymerizations of 15% solutions of BMMPHSu in MM by the use of curing system II (BP + L) (4%) + DMA(6%) + Co(1.5%) and curing system III L(6%) + DMA(10%) + Co(1.5%) were made.

The choice of curing system used for polymerization of films was made in such a way that not only gelation times but also the mass of curing system in comparison to the mass of BMMPHSu solution were taken into consideration.

Polymerizations were performed between two glass panels which were 2 mm apart and the obtained films were heated 4 h at 80°C.

Three polymerizations of 15% solution BMMPHSu using curing systems I, II and III, of the concentrations mentioned above, were also made but these films were not heated.

TABLE 6 Mechanical Properties of the Films

Film % of BMMPHSu	Curing system	Elongation [%]	Tensile strength [MPa]	MY	Hardness	
					Brinnell [MPa]	Shore D
15	BP + DMA	5.27	68.99	1131.1	167.4	81.2
10	BP + DMA	4.46	64.4	1322.5	164.2	81.4
5	BP + DMA	3.26	60.6	1451	161.8	81.9
15	BP + DMA*	6.1	68.3	1466.4	160.4	80.8
15	L + DMA + Co	3.9	52.7	1863.0	81.2	81.3
15	L + DMA + Co*	4.1	47.7	1844.2	75.6	76.1
15	(BP + L) + DMA + Co	5.8	54.0	1195.9	131.6	83.5
15	(BP + L) + DMA + Co*	6.5	49.9	1324.3	105.4	80.1

*Films not heated.

Mechanical Properties

The films were cut in stripes. The dimensions of stripes were $180 \times 10 \times 2$ mm. The stripes were subjected to tests for mechanical properties such as elongation at break, tensile strength and Young's modulus. Measurements were made using the TIRA-test 2200 (Germany), Brinnell's hardness by Koegel (Germany) and Shore's hardness using the Zwick (Germany) apparatus. The obtained results are presented in Table 6.

Thermal Analysis

Thermogravimetric analysis of the films was carried out using the Paulik-Erdey MOM derivatograph (Hungary). The thermal resistance of the films was examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial exothermic effect, temperatures of 5% and 10% weight loss and percentage mass loss at 200°C – 350°C were defined from the curves. Samples (0.1 g) were heated to 1000°C at a heating rate of 10 K/min.

Measurements of glass transition temperatures of the films were made using differential scanning calorimeter NETZSCH DSC 200 (Germany). Samples (3.9–11 mg) were heated from 0°C to 200°C at a heating rate of 10 K/min. The numerical data of thermal analysis are presented in Table 7.

TABLE 7 Thermal Properties and Temperature of Glass Transition of the Films

Film % of BMMPHSu and curing systems	Initial exothermic effect of decomposition [°C]	Mas loss		Mass loss at temperature				T _g [°C]
		5%	10%	200 [°C]	250 [°C]	300 [°C]	350 [°C]	
15 BP + DMA	230	290	300	0	0	10	50	132.9
10 BP + DMA	240	290	300	0	0.5	10	48	112.3
5 BP + DMA	220	280	300	0	0	10	50	111.3
15 BP + DMA*	250	290	300	0.5	0.75	10	55	110.8
15 L + DMA + Co	220	300	330	0.5	1	3	17	111.7
15 L + DMA + Co*	225	230	300	1.5	5.5	10	22	105.8
15 (BP + L) + DMA + Co	280	305	335	0	0.5	2	16	117.8
15 (BP + L) + DMA + Co*	280	320	340	0	0.75	2	12	130.5

*Films not heated.

RESULTS AND DISCUSSION

Table 1 presents gelation times for the polymers containing 15% of BMMPHSu obtained by the use of curing system I (BP + DMA). From these data one can see that for the highest concentration of curing system, gelation times are rather short and do not exceed 20 minutes. Table 1 also includes the gelation time of pure methyl methacrylate polymerized in the presence of the curing system BP(8%) + DMA(6%) (sample 5.0). In this case the gelation time is much longer than those of the compositions containing BMMPHSu.

Table 2 includes the gelation times of copolymers containing 15% of BMMPHSu obtained by the use of curing system II. In this system the peroxide component is a mixture of BP and L at the ratio of 1:1 by weight. The obtained results show that these gelation times are much longer than those obtained when curing system I is used. One may notice that if the concentration of DMA is below 6% or if the concentration (BP + L) is above 6% in the curing system the gelation times become longer.

The gelation times for the copolymers obtained by the use of curing system III presented in Table 3 are long and generally exceed 4 h. These gelation times are distinctly longer than those obtained by the use of curing systems I and II, although the concentration of L and DMA in this curing system are higher than those of curing systems I and II.

The data in Table 4 show that by the use of the same curing system gelation times are shorter for the composition containing more BMMPHSu.

Table 5 shows the peak exotherm temperatures for 4 samples containing 15% of BMMPHSu. For these samples curing system I with various concentrations of DMA (2% to 8%) and the constant concentration of BP were used. The obtained results show that the temperatures change in a narrow range (from 130 to 143.5°C). Temperature of polymerization decreases with the decrease of DMA concentration.

The results of mechanical tests presented in Table 6 show that elongation at break changes in the range from 3.26% to 6.5%. It should be noticed that if the same curing system were used, elongation would be slightly greater for in heated film samples. The smallest differences are observed for the samples cured by system III.

Tensile strengths of the films are in the range from 47.7 MPa to 86.99 MPa. Copolymers cured by curing system I show higher tensile strength than the others. Differences in tensile strength values for the in heated and heated samples are rather small (if the same curing system is used).

Young's modulus (MY) of tested films is in the range from 1131.2 to 1863.0. The samples cured by system III exhibit the highest value of MY. Brinnell's hardness of the films changes from 75 MPa to 167.4 MPa. The lowest values of hardness are obtained for the samples cured by system III whereas the highest values show films cured by system I. The obtained data in Table 6 also show that the films cured by curing system I show better mechanical properties than the others and that these properties depend on the concentration of BMMPHSu in copolymers.

From the data in Table 7 one can see that the curing system has an effect not only on gelation times but also on the thermal properties of the copolymers. The temperatures of initial exothermic effect of decomposition for the films are in the range of 220–280°C. The highest values of these parameters and the lowest mass loss at 350°C are exhibited by the films obtained by the use of curing systems II and III.

Glass transition temperatures of the obtained copolymers are slightly different. Their values change in the range from 105.8 to 132.9°C.

All the obtained copolymer films are transparent. The films obtained by the use of curing system I are slightly coloured. However, those obtained by the use of curing systems II and III are more intensively coloured.

REFERENCES

- [1] *Japan Pat. 81/39,256* (1981).
- [2] *Japan Pat. 85/29,237* (1985).
- [3] Inoue Hiroshiki, Matsukawa Kimihiro, Ueda Ahira and Nagai Susunu, *Osaka Munic. Tech. Res. Inst.*, Osaka Japan 536, Kagata to Kogyo (Osaka) (1990), **64**(3), 106–13.
- [4] *Japan Pat. 92/184,649* (1992).
- [5] *US Pat. 2508816* (1950).
- [6] *Japan Pat. 89/68,030* (1989).
- [7] S. Słomkowska *Chemia polimerów, Polimery biomedyczne*. Warsaw, 1998.
- [8] *EP Pat. 424,099* (1991).
- [9] *Japan Pat. 91/14,249* (1991).
- [10] *Japan Pat. 95/160,860* (1995).
- [11] *Japan Pat. 94/270,770* (1994).
- [12] *Japan Pat. 95/186,186* (1995).
- [13] *Japan Pat. 89/40,605* (1989).
- [14] *Japan Pat. 89/40,604* (1989).
- [15] *Japan Pat. 93/277,738* (1993).
- [16] *Japan Pat. 92/334,761* (1992).
- [17] *Hung. Pat. 48,917* (1989).
- [18] Rudź, W. and Podkościelny, W., Copolymerization of bis(4-methacryloylmethyl phenyl)-sulphone with styrene, *Inter. J. Polymeric Mater.* (in press).