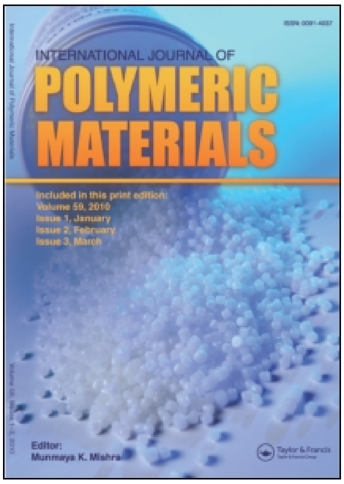

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

SYNTHESIS OF TERPOLYMER METHYL METHACYLATE-STYRENE-BIS(4-METHACRYLOYLMETHYLPHENYL)-SULPHIDE

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To cite this Article Rudź, Wieslaw and Podkościelny, Wawrzyniec(2004) 'SYNTHESIS OF TERPOLYMER METHYL METHACYLATE-STYRENE-BIS(4-METHACRYLOYLMETHYLPHENYL)-SULPHIDE', International Journal of Polymeric Materials, 53: 4, 355 — 364

To link to this Article: DOI: 10.1080/009140304904259861

URL: http://dx.doi.org/10.1080/009140304904259861

International Journal of Polymeric Materials, 53:355–364, 2004

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490429861

SYNTHESIS OF TERPOLYMER METHYL METHACYLATE-STYRENE-BIS(4-METHACRYLOYLMETHYLPHENYL)-SULPHIDE

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Bis(4-methacryloylmethylphenyl)-sulphide (BMMPhS) was used as a third monomer to obtain terpolymers containing also methyl methacrylate (MM) and styrene (St). Copolymerization was carried out using two curing systems, the first consisting of benzoyl peroxide (BP) and NN-dimethylaniline (DMA) and the second one consisting of luperox (L), dimethylaniline and cobalt naphthenate (Co).

Curing systems were examined as follows: 40% solution of BMMPhS in the mixed solvent MM-St (50:50) was polymerized and gelation times were measured at room temperature. Concentration of one component of the curing system was changed but the others were kept at the constant level.

The influence of BMMPhS concentration on gelation times was also determined. The curing systems I BP(6%) + DMA(6%) and II L(4%) + DMA(8%) + Co(2%) were used to determine this influence of BMMPhS concentration on gelation times. Using the two above–mentioned curing systems, polymerizations of the compositions containing 40% of BMMPhS and 60% of mixed solvent were made. Quantity of MM and styrene in the solvent was changed in the range from 10% to 90% by weight of each component. Based on the obtained results two curing systems were chosen and used for preparation of terpolymer films. The curing systems were the same as in the case of determining the influence of BMMPhS concentration on gelation times. Content of BMMPhS in the films was 40% compared to the solvent but the content of MM and styrene in solvent changed as follows: 90%MM-10%St, 75%MM-25%St, 50%MM-50%St, 25%MM-75%St and 10%MM-90% St., when curing system I was used, and 75%MM-25%St, 60%MM-40%St and 50%MM-50%St. in the case of curing system II.

Films of terpolymers were heated at 80°C for 4 h and next cut into stripes which were tested for mechanical properties like tensile strength, elongation at break, Young's modulus, hardness by Brinnell's method. Their thermal properties were also determined.

Received 23 July 2001; in final form 28 July 2001.

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Keywords: Terpolymers, MM-St-Bis(4-methacryloylmethylphenyl)-sulphide, unsaturated monomer BMMPhS, properties of the terpolymers

INTRODUCTION

Production of polymeric materials develops very dynamically. These materials play a more and more important role in industry and everyday life, and the demand for them grows constantly. Quantitative requirements for polymeric materials also increase. In spite of a large number of new polymers, only part of them found practical application. One can see that the amount of commercial polymeric materials increases, first of all, as a result of modification of polymers available for many years. Copolymerization is one of the ways to obtain new polymeric materials that have better properties and processing possibilities. Production of new polymeric materials is often based on one or more monomers obtained commercially. Styrene and methyl methacrylate are examples of monomers produced by commercial methods, which give copolymers with other vinyl-type monomers sufficiently readily. Numerous copolymers of styrene and methyl methacrylate are in commercial use and part of them found their place in student handbooks. Another part, which is less known, one can find in scientific literature. For example, these known and applied copolymers are as follows: styrene-methyl methacrylate known as SM [1–5], styrene-acrylnitrile (SAN), styrene-maleinic anhydride (SMA) [6–9], styrene-butadiene (Lipolit) or methyl methacrylate-acrylic acid [10] and methyl methacrylate-methyl acrylate [10], styrene-rubbers, methyl methacrylate-various four-functionality compounds, vinyl ethers or methyl methacrylate-vinyl chloride and styrene-divinylbenzene [11], styrene-α-methylstyrene [2], styrene-4-vinylpiridine [12], methyl methacrylate-α-methylstyrene [13], methyl methacrylate-acrylnitrile [14], styrene-ethylene (Arcel) [12]. Of course, besides those mentioned above two-component copolymers there is also large number of other copolymers, including styrene or methyl methacrylate. Studies on copolymers containing more than two monomers started a long time ago. These are terpolymers or multicopolymers. Until now, terpolymers have been applied more frequently. Nevertheless, multiple component copolymers are also obtained and some of them are manufactured for commercial purposes, e.g. methyl methacrylate-acrylnitrile-butadiene-styrene (Terlux) or acrylnitrile-ethene-methyl methacrylate-styrene-vinyl acetate obtained in Japan [15]. At present, researchers often focus their attention on the syntheses of terpolymers. As in the case of two-component copolymers, some terpolymers found practical application, e.g.: acrylnitrile-butadiene-styrene (ABS), methyl methacrylate-rubber-styrene (MBS) or methyl methacrylate-styrene-acrylnitrile (MSN). Many scientific papers describe less known and rarely applied terpolymers, e.g.: St-MM-2-hydroxyethyl methacrylate [16], St-divinylbenzene-MM [17], α-methylstyrene-AN-St [18], α-methylstyrene-St-acrylic acid [19], St-AN-chlorinated polyethylene [20], AN-St-acrylic acid esters, usually butyl acrylate (ASA), AN-St-AN-vinylcarbazol [10], MM-N-phenylmaleimide-St [21] or N-phenylmaleimide-St-AN [22].

In our previous papers we studied the influence of bis(4-methacryloylmethylphenyl)-sulphide (BMMPhS) on the properties of copolymers with styrene [23] and methyl methacrylate [24]. This paper deals with syntheses of terpolymers MM-St-BMMPhS. These studies are carried out in order to determine some of their mechanical and thermal properties.

EXPERIMENTAL

Materials

Methyl methacrylate (MM) was from Ventron (Germany); styrene, cobalt naphthenate (1% of Co in styrene) and N,N-dimethylaniline (10% solution in MM) were from POCh (Gliwice, Poland); Luperox (50% solution of methylethyl ketone hydroxyperoxide in dimethylphthalate) was from Luperox (Gunzburg, Germany); benzoyl peroxide (50% paste) came from "Organika-Sarzyna" Chemical Plant (Nowa Sarzyna, Poland); BMMPhS was obtained in our laboratory (MC-S University, Lublin Poland).

Polymerization

In order to determine the influence of curing system on gelation time, 40% solution of BMMPhS in the mixed solvent MM-St 50:50 was prepared. Methyl methacrylate and styrene were purified from inhibitors before their use. Polymerization of this solution was carried out by the use of two curing systems at room temperature, the first consisting of BP (benzoyl peroxide as a 50% paste) and DMA (10% solution of N,N-dimethylaniline in MM). Concentration of BP in the curing system changed in the range from 2% to 8% compared to the mass of solution. Concentration of DMA was kept on the stable level. Next, capacity of DMA in the curing system changed in the range from 2% to 8% and concentration of BP was stable. Efficiency of the curing system was determined based on the gelation time of composition consisting of curing system and 40% solution of BMMPhS in the mixed solvent

MM-St 50:50 at room temperature. The obtained results are summarized in Table 1.

Next, by the use of the same solution as in curing system I, gelation times of polymerization using curing system II were determined. Curing system II consisted of L (50% solution), DMA (10% solution) and Co (cobalt naphthenate 1% solution of Co). The curing system was investigated in such a way that one component of the curing system was changed but two were kept constant. Concentration in the curing system of L and DMA changed from 4% to 10% relative to the solution weight. Next, using the stable concentration of L 4% and DMA 8% in the curing system, influence of Co concentration from 2% to 6% on gelation time of the composition was determined. The obtained results are shown in Table 2.

The influence of BMMPhS concentration in the composition on the gelation time was also determined. Concentration of BMMPhS

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

Sample	40% solution of BMMPhS in MM + St(1:1) [g]	BP [g]	DMA [g]	Gelation time [min]
1	0.999	0.100	0.100	26
2	1.000	0.100	0.080	27
1.1	1.000	0.080	0.082	31
1.2	0.999	0.080	0.059	33
1.3	0.998	0.080	0.040	38
1.4	1.002	0.080	0.021	47
2.1	1.003	0.06	0.081	37
2.2	1.002	0.060	0.060	33
2.3	1.004	0.060	0.041	38
2.4	1.003	0.060	0.021	45
3.1	1.002	0.040	0.082	39
3.2	0.998	0.040	0.060	36
3.3	1.001	0.040	0.041	42
3.4	1.004	0.040	0.022	53
4.1	0.997	0.020	0.080	63
4.2	1.004	0.020	0.063	48
4.3	0.996	0.021	0.042	48
4.4	1.003	0.019	0.021	100
5*	1.001	0.100	0.100	4 days

BMMPhS-bis(4-methacryloylmethylphenyl)-sulphide.
BP-benzoyl peroxide (paste).
DMA-NN-dimethylaniline (10% solution).
MM-methyl methacrylate.
St-styrene.
*sample without BMMPhS.

TABLE 2 Influence of the Curing System L + DMA + Co on Gelation Times

Sample	40% solution of BMMPhS in MM:St(1:1) [g]	L [g]	DMA [g]	Co [g]	Gelation time [min]
6.1	1.004	0.100	0.100	0.019	192
6.2	1.000	0.099	0.098	0.020	196
6.3	1.000	0.101	0.100	0.21	269
6.4	0.998	0.098	0.099	0.020	247
7.1	1.003	0.081	0.100	0.022	174
7.2	1.004	0.079	0.080	0.022	188
7.3	1.002	0.079	0.060	0.019	206
7.4	1.001	0.082	0.042	0.019	239
8.1	0.999	0.060	0.101	0.021	203
8.2	1.000	0.062	0.080	0.020	202
8.3	1.004	0.061	0.061	0.021	220
8.4	0.998	0.060	0.059	0.019	241
9.1	0.998	0.040	0.100	0.021	185
9.2	0.999	0.041	0.081	0.021	187
9.3	1.004	0.040	0.059	0.021	199
9.4	1.004	0.041	0.043	0.021	205
10.1	1.002	0.040	0.079	0.021	180
10.2	1.003	0.041	0.081	0.040	174
10.3	0.998	0.041	0.079	0.061	162
11*	1.002	0.040	0.081	0.021	1 week
12**	1.003	0.100	0.101	—	—

L-luperox (50% solution).
Co-cobalt naphthenate (solution 1% Co).
*sample without BMMPhS.
** sample without Co.

changed from 20% to 60% relative to the solvent weight and the two curing systems I NB(6%) + DMA(6%) and L(4%) + DMA(8%) + Co(2%) were used. The results are shown in Table 3.

Besides, using these two curing systems, an influence of capacity of MM and St in composition on the gelation time was determined. Quantities of MM and St in the solvent changed from 10 to 90%. The obtained results are presented in Table 4.

The choice of curing system used for polymerization of terpolymers films was made in such a way that not only gelation time but also the mass of curing system in comparison to the mass of BMMPhS solution were taken into consideration. The polymerization of films were made using curing systems I and II, mentioned above, concentration of BMMPhS was 40% but capacity of MM and St in the solvent changed as follows: 90%MM-10%St, 75%MM-25%St, 50%MM-50%St, 25% MM-75%St, and 10%MM-90%St in the case of curing system I and 75%

TABLE 3 Influence of BMMPhS Concentration on Gelation Times

Sample	Concentration of BMMPhS in solvent MM:St (1:1)	Gelation time [min]	
		BP + DMA	L + DMA − Co
1	20	98	527
2	30	48	247
3	40	39	182
4	50	33	136
5	60	21	89

Curing system I -BP(6%) + DMA(6%).
Curing system II −L(4%) + DMA(8%) + Co(2%).

MM, 60%MM or 50%MM when curing system II was used. Terpolymers films were heated using the laboratory dryer for 4 hrs at 80°C, and then cut into stripes.

Mechanical Properties

The size of stripes was 180 × 10 × 1 mm. The stripes were subjected to mechanical properties tests such as elongation at break, tensile strength and Yuong's modulus. Measurements were made using the TIRA-test 2200 (Germany), Brinnell's hardness by Koegel (Germany). The obtained results are presented in Table 5.

TABLE 4 Influence of MM and Styrene Concentration in Composition on Gelation Times

Sample	Contents of solvent [%]		Gelation time [min] for system	
	St	MM	BP + DMA	L + DMA + Co
1	–	100	7	333
2	10	90	14	210
3	20	80	20	231
4	30	70	25	226
5	40	60	30	193
6	30	70	33	187
7	60	40	32	189
8	70	30	38	190
9	80	20	35	167
10	90	10	32	165
11	100	–	29	140

Thermal Analysis

Thermogravimetric analysis of the films was made using the Paulik-Erdey MOM derivatograph (Hungary).

The thermal resistance of the films was examined by differential analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial exothermic effect, temperatures of 5% and 10% weight loss and percentage mass loss at 200–350°C was determined from the curves. The 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). The samples (4.3–15 mg) were heated from 0°C to 200°C at a heating rate of 10 K/min. The numerical data of thermal analyses are presented in Table 6.

RESULTS AND DISCUSSION

In Table 1 gelation times for 40% solution of BMMPhS, in the mixed solvent MM-St (1:1), obtained with curing system I (BP + DMA) are shown. The concentration of BP and DMA in the curing system changed in the range from 2 to 6% by weight. From these data one can see that for the highest concentration of curing system, gelation time of sample 1 is only a little shorter than in the cases of samples 2 and 1.1. This was the reason that in the next experiments lower concentrations of BP and DMA were used. Generally, gelation times

TABLE 5 Mechanical Properties of the Terpolymer (BMMPhS-St) Films

Sample	Composition:* BMMPhS 40% Solvent (MM + St) 60%	Curing system	Elongation [%]	Tensile strength [MPa]	MY	Hardness Brinnell's [MPa]
1	90%MM + 10%St	BP + DMA	1.9	22.5	1297	123.8
2	75%MM + 25%St	BP + DMA	2.1	24.4	1297	132.0
3	50%MM + 50%St	BP + DMA	3.1	35.7	1283	119.6
4	25%MM + 75%St	BP + DMA	2.3	25.0	1248	115.8
5	10%MM + 90%St	BP + DMA	2.0	21.7	1223	118.7
6	75%MM + 25%St	L + DMA + Co	4.6	44.8	1221	100.5
7	60%MM + 40%St	L + DMA + Co	5.3	45.6	1283	83.7
8	50%MM + 50%St	L + DMA + Co	6.8	43.7	1050	90.1

*Compositions for the obtained films: 40% of BMMPhS and 60% of mixed solvent + curing system.

TABLE 6 Thermal Properties and Temperature of Glass Transition of the Films

Film	Initial exothermic effect of decomposition	Mass loss		Mass loss at temperature					Tg
		5 %	10%	200 [°C]	250 [°C]	300 [°C]	350 [°C]	400 [°C]	[°C]
90MM10St I	150	265	300	1	3	8	30	60	122.8
75MM25St I	170	280	305	1	3	8	33	63	112.7
50MM50St I	160	270	320	2	4	7	22	52	106.6
25MM75St I	160	250	330	2	4	7	13	37	111.2
10MM90St I	170	270	340	1	4	6	12	45	116.1
75MM25St II	160	280	320	1.5	4	7	20	45	113.7
60MM40St II	160	280	320	1	3	6	19	43	88.3
50MM50St II	160	270	320	1.5	4	7	15	40	68.8

I and II = curing systems.

Film = contents of MM and St in solvent and curing system.

Each polymerized composition consists of 40%BMMPhS and 60% mixed solvent MM and St + curing system.

were in the range from 30 to 45 min. except for the samples 1.4, 3.4, 4.1 and 4.4, for which concentration of BP and DMA in the curing system was low. The longest gelation time was of the sample 4.4 where concentration of BP and DMA in curing system I was 2% relative to the weight of solution of BMMPhS in mixed solvent MM-St (50:50). It is interesting to note that sample 4.4 (the lowest concentration of curing system I) showed the gelation time 100 min. but sample 5* (without BMMPhS) 4 days.

Table 2 includes the gelation times of terpolymers obtained by the use of curing system II. In this system concentration of L and DMA changed in the range 4–10% and concentration of Co from 2 to 6%. Influence of Co concentration was investigated in the way that concentration of L 4% and DMA 8% was in the curing system in each experiment. In the case of curing system II gelation times are much longer than in the case of curing system I. The results for the samples 10.1, 10.2 and 10.3 show that change of Co concentration have rather small influence on the gelation time of compositions.

Sample 11* shows that gelation time is very long for the composition without BMMPhS but sample 12** shows that curing system II doesn't work in the absence of Co.

The data in Table 3 show that by the use of the same curing systems I and II gelation times are shorter for the compositions containing more BMMPhS.

Table 4 includes the gelation times of terpolymers obtained by the use of curing systems I and II. In each case of polymerization, 40% solution of BMMPhS and 60% of mixed solvent MM-St was used. Contents of MM and styrene in the solvent changed from 10 to 90% by weight. The gelation times for the terpolymers obtained by the use of curing system I show small differences when the contents of styrene in the solvent is in the range from 40 to 90%. It should be noted that the increase of styrene contents from 0 to 50% in the solvent causes the prolongation of gelation time. When curing system II is used one can see that generally, the increase of styrene contents in the composition affects the decrease of gelation times. It follows from Table 4 that the gelation time for the two-component composition MM-BMMPhS is the shortest, if curing system I was used, and the longest in the case of curing system II.

The results of mechanical tests presented in Table 5 show that terpolymer films obtained by the use of curing system II are characterized by higher value of elongation and tensile strength but lower value of Brinnell's hardness than these obtained by the use of curing system I. Young's modulus of all tested films is similar. Besides, the films cured by both curing systems show the increase of elongation at break and tensile strength when the styrene content increases up to 50%. The value of Brinnell's hardness, generally, drops when styrene content increases in the composition.

It follows from the data presented in Table 6 that thermostabilities of all films are similar. Mass loss at the temperature 300°C is in the range from 6 to 8% and the temperature of initial exothermic effect of decomposition is in the range from 150 to 170°C. In the case of films cured using curing system I there should be noticed a small decrease of thermostability when the amount of MM in films increases. It is clearly seen when temperature of 10% mass loss and mass loss at temperatures of 350 and 400°C is taken into consideration. Glass transition temperatures of the obtained terpolymers are in the range from 68.8 to 122.8°C. Most Tg's are higher than 100°C.

All the obtained terpolymer films are transparent and very slightly colored.

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