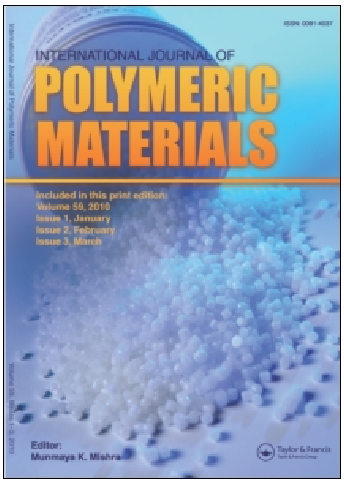

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SYNTHESIS OF THE TERPOLYMER METHYL METHACRYLATE-STYRENE-BIS(4-METHACRYLOYLMETHYLPHENYL)-SULPHONE

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Bis(4-methacryloylmethylphenyl)-sulphone (BMMPhSu) was employed as one of three monomers used for obtaining the terpolymer MMA-St-BMMPhSu. The influence of curing systems: benzoyl peroxide (BP) and NN-dimethylaniline (DMA), [system I] and luperox (L), NN-dimethylaniline and cobalt naphthenate (Co), [system II], on gelation time of 20% solution of BMMPhSu in the mixed solvent methyl methacrylate (MMA) and styrene (St) used in 1 : 1 ratio was studied. Concentration of ingredients of curing systems was variable. The influence of concentration of BMMPhSu in the compositions, and concentration of MMA and St in the solvent, was also investigated. Compositions consisting of curing system and BMMPhSu solution in the mixed solvent MMA-St were polymerized by the use of the same curing system BP(4%) + DMA(6%). In this way six terpolymer films were obtained. The curing system L(6%) + DMA(8%) + Co(2%) was also used for polymerization of the above mentioned solutions, except the solvent containing 10% MMA, and additional 5 films of terpolymer were obtained. Films were heated at 80°C for 4 hrs and then next cut into strips. The strips were tested for mechanical properties like tensile strength, elongation at break, Young's modulus, Brinnell's and Shore's hardness. Their thermal properties and glass transition temperatures were also determined.

Keywords: terpolymers, MMA-St-Bis(4-methacryloylmethylphenyl)-sulphone, unsaturated monomer BMMPhSu, mechanical and thermal properties of terpolymers

INTRODUCTION

Polymeric materials are a subject of research in many laboratories because these materials play an important role in industry, medicine and everyday life. Numerous studies concern terpolymers and multicopolymers because these materials show interesting, sometimes

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specific and in many cases better properties than the classic commercial two-component polymers. The use of a third monomer in polymerization often allows for much better adjustment of those materials to exhibit expected properties, leading to better design of terpolymers. The influence of use of some monomers on copolymer properties is very well known; for example, butadiene in polymerization always increases impact strength value of polymeric materials.

For obtaining terpolymers very complex monomers are used. Some of these monomers are common but others are merely known or entirely new. Some of the terpolymers, for example ABS, MBS ASA or MSN, became classic polymeric materials. They are based on monomers manufactured on the commercial scale and their properties allow for their use in many domains of commerce. A number of studied terpolymers are based on one well known monomer, for example methyl methacrylate, and two less known monomers. Examples of these kinds of terpolymers are:

Terpolymers of methyl methacrylate, 1,3-bis(trimethylsilylisopropyl methacrylate as well as methacrylic acid and maleic anhydride, which are two new positive type photoresists [1].

Terpolymers composed of methyl methacrylate, methoxypolyethyleglycol methacrylate, and dimethylsiloxane methacrylate (which have blood compatibility [2]), or nickel containing terpolymer, have been synthesized by polymerization of methyl methacrylate, acrylic acid with acrylonitrile containing different concentrations of poly (nickel methacrylate). The authors carried out the studies of antimicrobial activity of this terpolymer [3].

In the chemical literature, papers on syntheses of terpolymers or copolymers consisting of quite new monomers are rare. Some papers report studies on synthesis, properties and application of terpolymers containing two well known monomers and one less known. Terpolymers consisting of styrene and methyl methacrylate as well as an additional third monomer belong to this group. Examples of terpolymers consisting of styrene, methyl methacrylate and third monomers are as follows: Terpolymer styrene, methyl methacrylate and isoprene [4,5] or styrene, methyl methacrylate and ethyl oxide [6]. These terpolymers belong to the group of star terpolymers. Another example of terpolymers based on MMA and styrene are terpolymers obtained by polymerization of styrene, methyl methacrylate and methylacrylate [7,8], St, MMA and 2-hydroxyethyl methacrylate [9] or St, MMA and N-phenylmaleimide [10]. Some of these terpolymers are widely applied. The macroporous terpolymer MMA, styrene and divinylbenzene [11] in chromatography; St, MMA and acrylonitrile [12] as a modifier of rheological behaviour and mechanical properties of blends obtained from chlorinated polyethylene; MMA, St and dibutyltin maleate [13] may be used as a polyfunctional PVC stabilizer or bigraft terpolymers with butadiene backbone and styrene and MMA, which may be used as an impact modifier [14].

In our previous paper [15] we studied the influence of bis (4-methacryloylmethylphenyl)-sulphide (BMMPhS) on the properties of terpolymers with styrene and methyl methacrylate. This paper deals with the synthesis of terpolymers MMA, styrene and bis (4-methacryloylmethylphenyl)-sulphone (BMMPhSu). These studies are carried out in order to determine some of their mechanical and thermal properties.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was from Ventron (Germany); styrene, cobalt naphthenate (1% of Co in styrene) and N,N-dimethylaniline (10% solution in MMA) were from POCh (Gliwice, Poland); Luperox (50% solution of methylethylketonehydroperoxide was from Luperox (Gunzburg, Germany); benzoyl peroxide came from "Organika-Sarzyna" (Poland); BMMPhSu was synthesized in MC-S University, Lublin, Poland.

Polymerization

The MMA and styrene used for preparation of solvent of BMMPhSu were first purified by treatment with 2N aqueous NaOH. Then, the influence of curing systems on gelation time of 20% solution of BMMPhSu in the 50 : 50 mixed solvent MMA-St was determined. In these experiments two curing systems were applied. The first consisted of benzoyl peroxide (BP) as a 50% paste with N,N-dimethylaniline (DMA) as a 10% solution in MMA. The other curing system consisted of 50% solution of methylethyl ketone peroxide (L), N,N-dimethylaniline (DMA) 10% solution and cobalt naphthenate as a solution containing 1% of cobalt (Co).

Concentration of BP and DMA in the curing system I (BP + DMA) changed in the range from 2 to 8% compared to the mass of solution. When one of the curing system components changed, the other one was kept at constant level. Gelation times of compositions consisting of 20% solution of BMMPhSu and the curing systems were measured at room temperature. The obtained results are presented in Table 1.

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

Sample	20% solution of BMMPhSu in MMA + St(1 : 1) [g]	BP [g]	DMA [g]	Gelation time [min]
1	1.002	0.100	0.100	52
1.1	0.999	0.079	0.080	68
1.2	0.997	0.079	0.063	68
1.3	0.996	0.079	0.041	75
1.4	1.002	0.081	0.019	89
2.1	0.998	0.061	0.082	69
2.2	1.001	0.059	0.058	72
2.3	1.003	0.060	0.038	73
2.4	0.998	0.061	0.024	80
3.1	1.004	0.040	0.083	73
3.2	1.000	0.040	0.062	72
3.3	1.000	0.040	0.040	78
3.4	1.000	0.040	0.020	88
4.1	1.002	0.021	0.081	84
4.2	1.001	0.020	0.062	81
4.3	0.996	0.020	0.038	86
4.4	1.003	0.020	0,021	99
5*	1.003	0.100	0.100	2 weeks

BMMPhSu-bis(4-methacryloylmethylphenyl)-sulphone
BP-benzoyl peroxide (paste)
DMA-NN-dimethylaniline (10%) solution
MMA-methyl methacrylate
St-styrene
*−sample without BMMPhSu (styrene + methyl methacrylate 1 : 1)

The curing system II (L + DMA + Co) was investigated in such a way that one component of the curing system was changed but two were kept at constant level. Concentration in the curing system of L and DMA changed from 4 to 10% in relation to the solution weight. Concentration of Co changed from 0 to 6% in comparison with the solution weight but the concentration L was constant 4% and DMA 8%. The obtained results are summarized in Table 2.

Concentration of BMMPhSu in the composition and its influence on gelation time was also determined. Content of BMMPhSu in the composition changed from 5 to 20% in relation to the solvent weight and the two curing systems, I BP(4%) + DMA(6%) and II L(4%) + DMA(8%) + Co(2%), used. The results are shown in Table 3.

Besides, using these two curing systems, the influence on gelation time of capacity of MMA and St in the composition was determined. Quantities of MMA and St in the solvent changed from 10 to 90%. The

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

Sample	20% solution of BMMPhSu in MMA-St (1 : 1) [g]	L [g]	DMA [g]	Co [g]	Gelation time [min]
6*	1.000	0.104	0.103	–	–
7.1	0.997	0.103	0.099	0.022	420
7.2	1.003	0.102	0.079	0.019	505
7.3	0.999	0.103	0.062	0.018	515
7.4	0.998	0.101	0.041	0.019	594
8.1	0.997	0.083	0.102	0.020	544
8.2	0.999	0.080	0.083	0.021	571
8.3	0.998	0.080	0.060	0.021	595
8.4	0.997	0.080	0.043	0.019	644
9.1	1.003	0.060	0.101	0.022	483
9.2	1.002	0.063	0.080	0.020	574
9.3	0.998	0.062	0.061	0.022	558
9.4	1.000	0.061	0.042	0.022	605
10.1	1.003	0.041	1.102	0.020	446
10.2	1.002	0.041	0.081	0.021	459
10.3	0.997	0.043	0.058	0.022	554
10.4	0.999	0.039	0.042	0.021	592
11.1	1.003	0.041	0.079	0.021	460
11.2	0.999	0.040	0.080	0.043	433
11.3	0.998	0.040	0.082	0.062	416
12**	1.003	0.040	0.100	0.020	–

L-luperox (50% solution).

Co–cobalt naphthenate (solution 1% of Co).

* - sample without Co.

** - sample without BMMPhSu.

TABLE 3 Influence of BMMPhSu Concentration on Gelation Time

Sample	Concentration of BMMPhSu in solvent MMA : St (1 : 1) [%]	Gelation time [min]	
		Curing system	
		BP + DMA	L + DMA + Co
1	5	900	1440
2	10	369	885
3	15	205	536
4	20	73	159

Curing system BP(4%) + DMA(6%).

Curing system L(4%) + DMA(8%) + Co(2%).

obtained results are presented in Table 4. Next, using the two curing systems I and II, terpolymer films were obtained. Concentration of BMMPhSu in each film was 20% relative to the solvent weight but the content of MMA and St in the solvent changed as follows: 90,75,60,50,25 and 10% MMA in the case of curing system I and 90,75,60,50 and 25% MMA when curing system II was used. Polymerizations were performed between two glass panels, which were 1 mm apart. In this manner eleven films were obtained, which were then heated for 4 hrs at 80°C and later cut into strips.

Mechanical Properties

The dimensions of strips were 180 × 10 × 1 mm. The strips were submitted to tests for mechanical properties such as Young's modulus, elongation and tensile strength using the TIRA-test 2200 (Germany), Brinnell's hardness by Koegel (Germany), and Shore's hardness using the Zwick (Germany) apparatus. The results are presented in Table 5.

Thermal Analysis

Thermogravimetric analysis of the films was conducted using the Paulik-Erdey MOM derivatograph (Hungary). The thermal resistance was examined by differential analysis (DTA) and thermogravimetric analysis (TGA). The temperature of initial exothermic effect,

TABLE 4 Influence of MMA and Styrene Concentration in the Solvent of BMMPhSu

	Contents of solvent [%]		Gelation time [min]	
Sample	St	MMA	BP + DMA	L + DMA + Co
1	10	90	43	403
2	20	80	62	416
3	30	70	68	434
4	40	60	70	435
5	50	50	73	459
6	60	40	85	451
7	70	30	98	435
8	80	20	110	412
9	90	10	121	394

20% solution of BMMPhSu in the mixed solvent was used.
Curing system BP(4%) + DMA(6%).
Curing system L(4%) + DMA(8%) + Co(2%).

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

Sample	Composition* BMMPhSu 20% Solvent 80% (MMA + St)	Curing system	Elongation [%]	Tensile strength [MPa]	MY [MPa]	Brinnell's hardness [MPa]	Shore's hardness scale D
1	90MMA + 10St	BP + DMA	14.6	55.7	732.3	116.2	84.0
2	75MMA + 25St	BP + DMA	4.8	50.6	1007.3	91.5	78.5
3	60MMA + 40St	BP + DMA	5.2	63.2	1903.5	112.3	83.5
4	50MMA + 50St	BP + DMA	11.1	54.2	836.0	104.9	82.0
5	25MMA + 75St	BP + DMA	5.3	61.6	1729.2	110.2	82.5
6	10MMA + 90St	BP + DMA	4.4	48.8	1329.0	93.2	80.5
7	90MMA + 10St	L + DMA + Co	4.1	43.1	522.5	101.4	78.2
8	75MMA + 25St	L + DMA + Co	9.3	46.8	845.8	82.9	77.1
9	60MMA + 40St	L + DMA + Co	5.2	56.0	537.2	98.7	78.5
10	50MMA + 50St	L + DMA + Co	4.0	33.1	1416.4	75.5	76.2
11	25MMA + 75St	L + DMA + Co	3.7	40.3	485.9	83.9	74.6

* -Compositions for the obtained films: 20% of BMMPhSu and 80% of the mixed solvent MMA + St and curing system.

temperatures of 5 and 10% weight loss and percentage mass loss at the temperatures from 200 to 400°C were determined from the curves. The temperatures of glass transition were measured by the use of differential scanning calorimeter NETZSCH DSC 200 (Germany). The results of thermal analyses are shown in Table 6.

RESULTS AND DISCUSSION

The data included in Table 1 show that gelation times of 20% solution of BMMPhSu in the mixed solvent MMA-St 50 : 50 are rather long (68–99 min). Sample 1 shows that the use of more concentrated curing system BP and DMA (both components 0.100 g) results only in a small change of gelation time; for that reason in the next experiments concentration of BP and DMA in the curing systems changed in the range from 2 to 8% (in relation to the mass of BMMPhSu solution). Gelation times in the case of curing system II (L + DMA + Co) are much longer than in the case of the curing system BP + DMA and they are from 7 to 10 hours. Samples 12* and 6 show that curing system II does not work in the case when the composition does not contain BMMPhSu or when curing system does not contain Co. On the other hand, concentration of Co in the curing system has a slight influence

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

Film, capacity of MMA in solvent + curing system	Initial exothermic effect of decomposition	Temperature of mass loss [°C]		Percentage of mass loss at temperature [°C]					Tg [°C]
		5%	10%	200	250	300	350	400	
90MMA* I**	120	150	190	2.5	5	12	36	66	108.9
75MMA I	110	210	280	4.5	8	11	21	43	108.3
60MMA I	150	270	320	1.5	4	8	20	49	108.2
50MMA I	140	260	310	2	4.5	7.5	18	45	109.0
25MMA I	150	260	300	2	4.5	9	24	53	105.2
10MMA I	130	205	280	4	9	12	21	46	109.7
90MMA II***	120	260	300	2	5	8.5	25	61	104.9
75MMA II	120	240	300	3	6	9.5	22	54	106.9
60MMA II	140	240	310	2.5	5.5	8.5	19	50	100.6
50MMA II	120	200	280	4.5	8	11	22	60	113.7
25MMA II	110	190	250	6	10	12.5	21	43	103.5

* 90MMA = Mixed solvent 90% of MMA and 10% of St.
I** Curing system BP + DMA.
II*** Curing system L + DMA + Co.

on the change of gelation times (samples 11.1; 11.2 and 11.3), therefore a concentration 2% Co by weight was applied in the next experiments.

The results in Table 3 show that under the same polymerization conditions the gelation time very strongly depends on the concentration of BMMPhSu in the composition. This kind of dependence appears for both curing systems. Table 4 includes the gelation times of terpolymers obtained by the use of curing system I BP(4%) + DMA(6%) and II L(4%) + DMA(8%) + Co(2%). In each polymerized solution the concentration of BMMPhSu was 20%. The contents of MMA and St in the solvent of BMMPhSu changed from 10 to 90% by weight. The gelation times for the terpolymers obtained by the use of curing system I increase systematically when the content of St increases in the solvent. In the case of curing system II the gelation times are about 400 minutes and the differences between them are small.

Mechanical properties of the obtained terpolymer films show strong differences. Elongation changes from 3.7% (sample 11) to 14.6% (sample 1). Similarly Young's modulus is from 485.9 to 1903.5 (sample 3), tensile strength from 33.1 MPa (sample 10) to 63.1 MPa (sample 3). Smaller differences are observed when Brinnell's and Shore's hardness are taken into consideration. Brinnell's hardness changes from 75.5 MPa (sample 10) to 116.2 MPa (sample 1) and Shore's hardness (scale D) from 74.6 (sample 11) to 84.0 (sample 1). One may notice, that the films cured by the use of curing system I show better mechanical properties than those cured by curing system II. The best mechanical properties are found in samples 3 (60MMA I) and 5 (25MMA I). If concentration of MMA in the solvent is taken into consideration one can see that the best mechanical properties are exhibited in the films containing 60% MMA and the worst films 50% MMA. In Table 6 where thermal properties of the obtained films are presented, one can see that the initial exothermic effect of decomposition is in the range from 110 to 150°C, temperatures of 5% mass loss are in the range 200 to 250°C, except for the films 90MMA I and 25MMA II, and temperatures of 10% mass loss (except for the same films) about 300°C.

For all films mass loss at the temperature 250°C is below 10%, and at 300°C below 13%. Generally, the best thermal resistance is found in the films 60MMA I and 60MMA II (compared with the films in their group). The film 50MMA I has also good resistance. Temperatures of glass transition of the obtained films are in the range from 100.6 to 113.7°C.

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