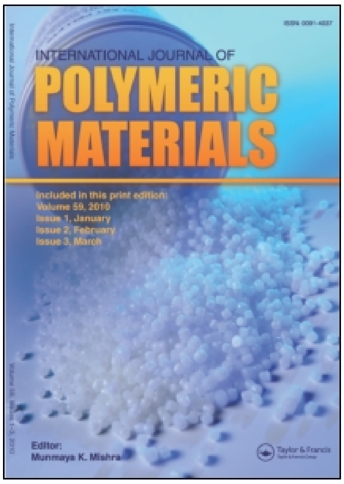

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Synthesis of 4-Methacryloylmethyldiphenylsulphone and its Copolymerization

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Synthesis of 4-Methacryloylmethyldiphenylsulphone and its Copolymerization

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This paper presents the synthesis of two new compounds: 4-chloromethylphenylsulphone (4-CmDPhSu) and 4-methacryloylmethylphenylsulphone (4-McMDPhSu) which are derivatives of diphenylsuphone. Introduction of the methacryloyl group into 4-CmDPhSu transferred this compound into the vinyl monomer 4-McMDPhSu. This monomer was polymerized and copolymerized with the use of two types of initiators: a mixture containing benzoyl peroxide (BP) and N,N-dimethylaniline (DMA), as well as the photoinitiators Irgacure 651 or Darocur 1173. In further studies, its copolymers with methyl methacrylate were used. Their thermomechanical properties were studied.

Keywords 4-chloromethylphenylsulphone, 4-methacryloylmethylphenylsulphone, copolymerization, monomers, properties of copolymers

INTRODUCTION

Production of polymeric materials belonging to the acrylic family develops very dynamically. The glasslike appearance and nonbreakable properties have made these plastics popular for the building, automotive, aerospace, and furniture industries. These materials are also often used in dentistry and medicine as denture plates, artificial teeth, or orthopedic cement [1]. Acrylic monomers can polymerize by a free radical addition reaction. Their polymerization runs rapidly in the presence of peroxide or azonitrile initiators. When the reaction is initiated by UV light or by electron beam its course is not so rapid and the properties of the final product can be easily controlled [2]. However, monomeric acrylates and methacrylates are relatively volatile, toxic,

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and have an unpleasant odor [3,4]. Oligomeric acrylates are much less volatile but exhibit high viscosities. Solid monomers obviously have lower toxicity.

In spite of these drawbacks acrylate and methacrylate monomers are commonly used. For the last thirty years these compounds have attracted the attention of both scientists and producers [5–9].

In this paper we present the synthesis and properties of the new methacrylic monomer 4-methacryloylmethyldiphenylsulphone (4-McMDPhSu). This monomer is in a solid state at room temperature. In its chemical structure it possesses the sulfonyl group. As this group is of deactivating character its presence has influence on the properties of the obtained polymers. To confirm this assumption polymerization and copolymerization of 4-McMDPhSu with methyl methacrylate were studied. The properties of the obtained polymers were compared with those of 4,4′-dimethacryloylmethylphenylsulphone copolymers [10,11].

EXPERIMENTAL

Reagents

Methyl methacrylate (MMA) was from Ventron (Germany), Irgacure 651 (2,2-dimethoxy-1,2-diphenylethen-1-one) and Darocur 1173 (2-hydroxy-2-methyl-1-phenylpropan-1-one) from Aldrich. Benzoyl peroxide (BP) 50% paste from Organika-Sarzyna, Poland. Styrene (St), N,N-dimethylaniline (DMA), benzene, S_2Cl_2, sulphuric acid, ethanol, methanol, hydrochloric acid, formaldehyde, H_2O_2 (30%)¸ acetic acid, $AlCl_3$, KOH, and hydroquinone came from POCh (Gliwice, Poland). Methacrylic acid, N,N-dimethylformamide (DMF), divinylbenzene (DVB), glicydyl methacrylate (GMA), acrylonitrile (AN), *2*-vinylpyridine (VP), N-vinylpirolidone (NVP) were from Fluka AG (Buchs, Switzerland).

Synthesis of 4-Methacryloylmethyldiphenylsulphone (4-McMDPhSu)

4-methacryloylmethyldiphenylsulphone was obtained as a result of the four-step synthesis shown in Figure 1.

In the first step, diphenyl sulphide was obtained in the Friedel-Crafts reaction of benzene with S_2Cl_2. Its purification was accomplished by vacuum distillation at 162–163°C/18 mmHg. Chloromethylation of diphenyl sulphide was carried out by adding concentrated sulphuric acid into a mixture of diphenyl sulphide, acetic acid, concentrated hydrochloric acid, and formaldehyde present in a three-necked flask. The sulphuric acid was added dropwise at 40°C over 3 h. When the reaction of addition was over, the content of the flask was stirred at 50°C for 5 h. Next, the obtained 4-chloromethyldiphenylsulphide

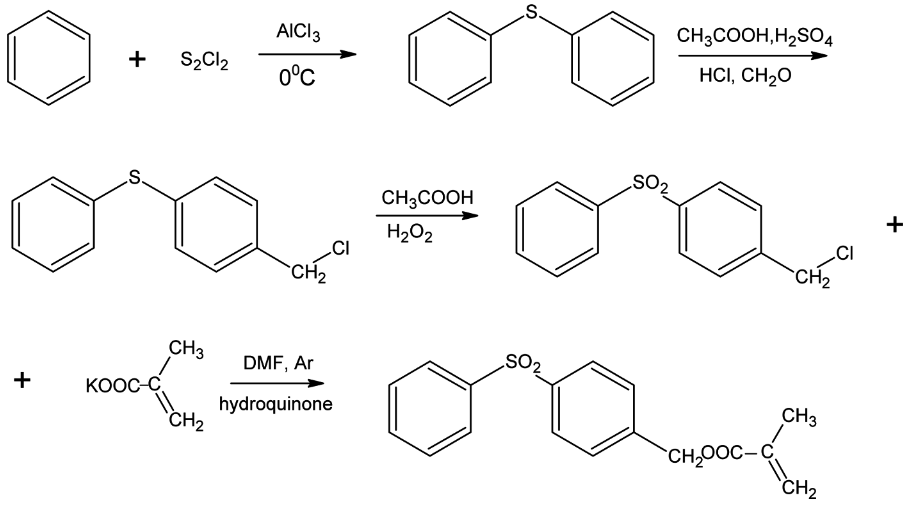


Figure 1: Synthesis of 4-methacryloylmethyldiphenylsulphone (4-McMDPhSu).

was separated and purified by distillation at a reduced pressure (136–138°C/0.1 mmHg) [12]. Then the compound was dissolved in acetic acid and oxidized by H_2O_2 at 85°C for 30 min while stirring [13]. Heating was continued for further 20 min. After cooling, precipitated 4-CmDPhSu was separated and recrystallized from ethanol. The melting point of this compound was 131–133°C. Yield 78%.

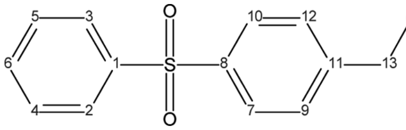
Next, the reaction between 4-CmDPhSu and potassium methacrylate was carried out. This reaction was carried out in a solution of DMF at its boiling point in the presence of hydroquinone and argon atmosphere [14]. The product, 4-methacryloylmethyldiphenylsulphone (4-McMDPhSu), was obtained in a yield of 72%. The melting point of the final compound after recrystallization from methanol (1 g/15 cm^3) was 118–120°C. Chemical structures of both new compounds (4-CmDPhSu and 4-McMDPhSu) were confirmed by elemental, IR, ^1H-NMR, and ^{13}C-NMR analyses. The results of elemental analysis are shown in Table 1 while those of NMR are shown in Tables 2 and 3.

Table 1: Elemental analysis of 4-CmDPhSu ($C_{13}H_{11}SO_2Cl$, MW 266.76) and 4-McMDPhSu ($C_{17}H_{16}O_4S$; MW316.371).

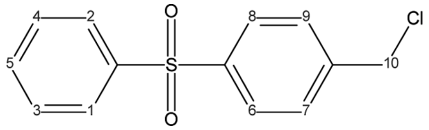
	Concentration (%)			
	Calculated		Found	
Compound	**C**	**H**	**C**	**H**
4-CmDPhSu	58.53	4.15	58.62	4.09
4-McMDPhSu	64.54	5.10	64.41	5.11

Table 2: NMR data of 4-CmDPhSu.

^{13}C-NMR



H-NMR



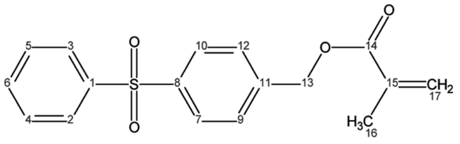
No. of atom C	Shift	No. of atom H	Shift
13	44.8	10	4.582
7,10	127.7	5	7.260
2.3	128.2	7,9	7.508
9,12	129.3	3,4	7.536
4.5	129.4	1,2	7.924
6	133.3	6,8	7.952
1	141.4		
11	141.6		
8	142.8		

Characterization

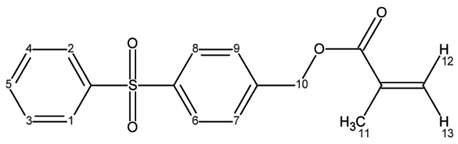
^{1}H and ^{13}C NMR spectra of 4-CmDPhSu and 4-McMDPhSu were recorded with a Brucker 300 MHz spectrometer (Brucker, Germany) at room temperature in deuterated chloroform ($CDCl_3$). Chemical shifts are reported relative to chloroform (δ 7.26) for ^{1}H NMR and chloroform (δ 77.28) for ^{13}C NMR.

Table 3: NMR data of 4-McMDPhSu.

^{13}C-NMR



^{1}H-NMR



No. of atom C	Shift	No. of atom H	Shift
16	18.3	11	1.96
13	65.1	10	5.22
17	126.4	12	5.62
7,10	127.7	13	6.16
2,3	128.0	5	7.48
9,12	128.3	7,9	7.50
4,5	129.3	3,4	7.53
6	133.3	1,2	7.93
15	135.8	6,8	7.96
11	141.3		
8	141.5		
1	141.8		
14	166.9		

Elemental analysis of the product was made on a Perkin-Elmer CHN 2400, while IR spectra were made on a Bio-Rad Excalibur 3000 with KBr pellets.

In the IR spectrum of 4-McMDPhSu the following bands (in cm^{-1}) are present: C–O 1699.6; SO_2 1323.5 and 1157.3; =CH_2 3065.4; C=C conjugated with CO 1631.8; CH_3 2966.7; C_{Ar}-H 3036.88. In this spectrum there was no frequency for $-CH_2Cl$ group.

4-McMDPhSu is a white crystalline compound with a melting point of 118–120°C. The solubility tests for 4-McMDPhSu showed that it is well-soluble in common solvents such as acetone, methanol, ethanol, 1,4-dioxane, ethylacetate, toluene, and acetic acid. It is insoluble in water. Solubility of this compound in solvents often used as monomers in copolymerization was also determined. It was established that 100 mg of 4-McMDPhSu is soluble in 400 mg of St (1:4), and in MMA (1:4), DVB (1:4), NVP (1:2), GMA (1:2), VP (1:3).

4-CmDPhSu is also a white crystalline compound with a melting point of 131–133°C. It is soluble in methanol, ethanol, acetone, acetic acid, chloroform, toluene, and insoluble in water.

Copolymerization

Copolymerizations were carried out by the two methods of radical polymerizations. 10 and 20% of 4-McMDPhSu were copolymerized with St, MMA, and NVP in the presence of benzoyl peroxide (BP) and N,N-dimethylaniline (DMA). BP(2%) + DMA(2%), BP(3%) + DMA(3%), and BP(4%) + DMA(4%) concentrations relative to the monomers solution (w/w) were used. Gelation times of these copolymers at room temperature were determined. Photopolymerization was carried out by the use of 2 lamps of 366 nm (Philips, TSM0022 TL-D18 W) at room temperature. The melted sample of 4-McMPhSu was irradiated to obtain homopolymer, and 10% solution of 4-McMDPhSu in MMA to prepare copolymers. As photoinitiators, Darocur 1173 (1%) and Irgacure 651 (1%) were used.

Thermal Properties

Thermal stability of the polymers was determined using the derivatograph MOM (Budapest, Hungary). The heating rate was 5°C/min, in air. The initial decomposition temperatures were determined from the course of the TG curves.

The calorimetric measurements were performed on a differential scanning calorimeter Netzsch DSC 200 (Netzsch, Germany). The conditions were as follows: sample weight ~5 mg, nitrogen atmosphere, sealed aluminium pans. An empty aluminium pan was used as a reference. The resins were cured in a scanning mode from 20 up to 400°C at 10 K/min heating rate. T_g values were taken from the second DSC run.

Mechanical Properties

To study the mechanical properties of the copolymers 4 foils were prepared. Two of them were copolymers containing 10 and 20% of 4-McMDPhSu, respectively. These copolymers were polymerized at 80°C for 4 h with the addition of a proper hardening system. The others, containing 10% of 4-McMDPhSu were polymerized in the presence of Irgacure 651 or Darocur 1173. Polymerization was carried out at room temperature between two glass panels. The obtained foils were heated at 80°C for 4 h and cut into strips of 180 × 10 × 2 mm.

Only 2 samples were obtained in a form suitable for mechanical studies. For them, Young modulus, elongation at break, and tensile strength were measured using TIRA-test 2200 (Germany). Shore's hardness was determined by the use of the Zwick apparatus.

RESULTS AND DISCUSSION

In the previous studies synthesis and properties of 4,4′-dimethacryloylmethylphenylsulphone and its copolymers were presented [10,11]. Now, we present a new monomer which is also a derivative of diphenylsulphone but contains only one methacrylic group in its chemical structure.

To study its tendency for polymerization, the solutions of St, MMA, and VP containing 10 and 20% of 4-McMDPhSu were prepared and polymerized at room temperature in the presence of BP + DMA. It proved that in the presence of BP + DMA (2% + 2%) none of the copolymers was formed during 48 h. In the presence of BP + DMA (3% + 3%) polymerization with St and NVP also did not occur during 48 h. The copolymer containing 10% of 4-McMDPhSu in MMA was obtained after 210 min, while that containing 20% after 50 min.

To shorten polymerization times, increased concentrations of initiators were applied. Copolymerization with MMA was carried out in the presence of BP + DMA (4% + 4%). The copolymers containing 10 and 20% of 4-McMDPhSu were obtained after 160 and 25 min respectively (Table 4).

The photopolymerization reaction of 4-McMDPhSu was also carried out. The samples of 4-McMDPhSu were exposed to UV light of 2 lamps in distance of 20 cm. The sample of melted 4-McMDPhSu without any photoinitiator polymerized after 90 min. When Darocur 1173 or Irgacure 651 was added homopolymerization took place after ca. 2 min.

We also attempted to obtain its 10% copolymer in MMA by the use of UV light. It proved that with Irgacure 651 (1%) the polymerization took 40 min. The addition of Darocur 1173 (1%) significantly shortened the polymerization time but the obtained product was very brittle.

In Table 5 the mechanical properties of the obtained copolymers are presented. The studied copolymers are characterized by lower hardness and

Table 4: Polymerization conditions.

Sample no.	Concentration of 4-McMDPhSu (%)	Solvent	Initiator	Gelation time (min)
1	10	MMA	BP + DMA	160
2	20	MMA	BP + DMA	25
3	10	MMA	Irgacure 651	40
4	10	MMA	Darocur 1173	6
5	100	–	Irgacure 651	2
6	100	–	Darocur 1173	2

tensile strength than those of 4,4′-dimethacryloylmethylphenylsulphone [10,11]. Their Young modulus has comparable values. On the other hand, their elongations at break are smaller than that of poly(MMA) while the glass transition temperature for the sample polymerized in the presence of BP + DMA (4% + 4%) is significantly higher. T_g for this copolymer is 126°C. According to Wanderlich [15]. T_g for poly(MMA) is 105°C. Values of T_g for the copolymers of the same concentration of 4-McMDPhSu polymerized in the presence of Irgacure 651 and Darocur 1173 indicate that copolymerization was not completed.

The studies of thermal stabilities, presented in Table 6, confirmed this assumption. The initial decomposition temperature for the copolymer obtained in the presence of BP + DMA (4% + 4%) is higher than those obtained for the photoinitiated copolymers. The data also show that poly(McMDPhSu) is thermally stable. The initial decomposition temperatures for the samples polymerized in the presence of Irgacure 651 and Darocur 1173 are 210 and 260°C, respectively.

The results presented here show that the studied new monomer, 4-methacryloylmethylphenylsulphone, is less reactive in copolymerization reactions than 4,4′-dimethacryloylmethylphenylsulphone. In the presence of BP + DMA, high concentrations of initiators are necessary for its polymerization. In the presence of photoinitiators, the copolymerization runs more quickly but this process is not completed.

Table 5: Mechanical properties of the copolymers of 4-McMDPhSu.

Sample no.	Elongation at break (%)	Tensile strength (MPa)	Young modulus (MPa)	Tg (°C)	Shore's hardness (MPa)
1	3.9	43.9	1219	115.5	45.4
2	3.1	42.3	1178	126.0	62.2
3	–	–	–	79.5	58.4
4	–	–	–	89.9	70.0
5	–	–	–	107.4	–
6	–	–	–	105.0	–

Table 6: Thermal properties of the studied polymers.

Sample no.	Initial decomposition temperature (°C)	Percentage of mass loss at temperature (°C)			
		200	250	300	350
1	150	5	9	20	65
2	170	3	7	18	65
3	140	6	10	20	45
4	150	3	25	55	–
5	210	0	2	8	20
6	260	0	0	2	9

CONCLUSION

The obtained results showed that 4-McMDPhSu is rather unreactive in polymerization reactions. Probably the presence of sulfonyl group in the chemical structure deactivated this compound.

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