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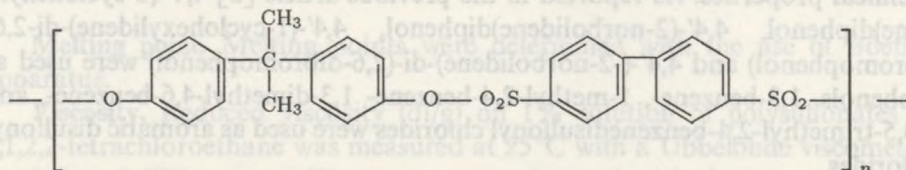
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**Linear Polysulfonates. II\*. Products of 4,4'-(1-Cyclohexylidene)diphenol and 4,4'-(2-Norbolidene)diphenol with Some Aromatic Disulfonyl Chlorides**

Liniowe polisulfoniany. II\* Produkty polikondensacji 4,4'-(1-cykloheksylideno)difenolu i 4,4'-(2-norbolideno)difenolu z niektórymi aromatycznymi disulfochlorkami

INTRODUCTION

The reaction of interfacial polycondensation of aromatic diphenols with aromatic disulfonyl chlorides in the presence of quarternary ammonium salts as a catalyst to obtain aromatic polysulfonates is described in some patents and papers [14]. Diphenols of the type bisphenol A and 4,4'-diphenyl, 4,4'-diphenylether, 4,4'-diphenylmethane, 1,3-benzene, 2,4-toluenedisulfonyl chlorides as aromatic disulfonyl chlorides are used in the reaction. The typical structure of aromatic polysulfonates is as follows:



Aromatic polysulfonates possess good physical, chemical, and electrical properties. These polymers are characterized by high melting temperatures and good chemical stability. While resistant to alkali acids, and oils, they are, however, soluble in halogenated aliphatic hydrocarbons which permit for film and fiber formation from solutions. Conventional techniques of thermoplastic

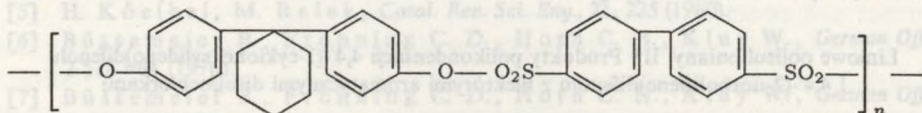
\* For Paper I see Ref. 5. Patrz [5].

treatment such as: extrusion, injection moulding, and pressing are also possible.

New aromatic (poly)cycloaliphatic polysulfonates of good physical, chemical, and thermal properties were described [5]. It was found that polysulfonates of high molecular weight could be easily obtained by interfacial polycondensation of aromatic (poly)cycloaliphatic diphenols with aromatic disulfonyl chlorides.

4,4'-(1-Cyclohexylidene) diphenol, 4,4'-(-norboldiene) diphenol, 4,4'-(1-cyclohexylidene)-di-(2,6-dibromophenol) and 4,4'-(2-norboldiene)-di-(2,6-dibromophenol) were used as diphenols. Diphenyl 4,4'-, diphenylether 4,4', -diphenylthioether 4,4'-, and diphenyl methane 4,4'-disulfonyl chlorides were used as aromatic disulfonyl chlorides.

The typical structure of polysulfonates obtained in the reaction is presented by the formula:

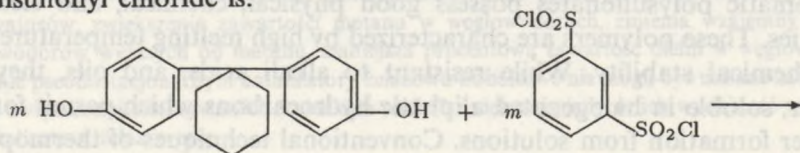


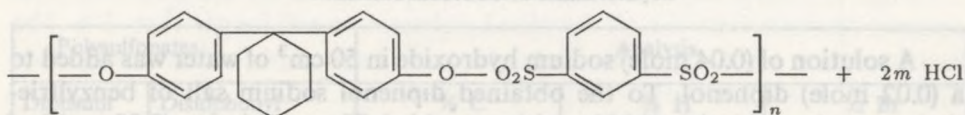
The polysulfonates were found to have a low degree of crystallinity, softening ranges in the region 180–310°C and molecular weight in the region:  $\bar{M}_n$  3,190–4,420, and  $\bar{M}_w$  19,900–83,370, thermal stability to above 300°C, and reduced viscosities in the range 0.2–1.00 dl/g.

The polymers obtained are soluble in low-boiling organic solvents which is profitable for their use.

Taking into consideration the properties of polysulfonates described above, it seemed to be interesting to synthesize new aromatic (poly)cycloaliphatic polysulfonates, to determine their structure and to define some physical and chemical properties. As reported in the previous article [5] 4,4'-(1-cyclohexylidene)diphenol, 4,4'-(2-norboldiene)diphenol, 4,4'-(1-cyclohexylidene)-di-2,6-(bromophenol) and 4,4'-(2-norboldiene)-di-(2,6-dibromophenol) were used as diphenols. 1,3-benzene-, 1-methyl-2,4-benzene-, 1,3-dimethyl-4,6-benzene-, and 1,3,5-trimethyl-2,4-benzenedisulfonyl chlorides were used as aromatic disulfonyl chlorides.

The reaction scheme (I) for 4,4'-(1-cyclohexylidene)diphenol and 1,3-benzenedisulfonyl chloride is:





## EXPERIMENTAL

## REAGENTS

The below mentioned aromatic (poly)cycloaliphatic diphenols were obtained by the reaction described in the literature.

The following aromatic disulfonyl chlorides were obtained by direct chlorosulfonation of adequate hydrocarbons or in the reaction of sodium or potassium salts of arylodisulfonic acid with  $\text{PCl}_5$ .

4,4'-(1-Cyclohexylidene)diphenol (diphenol C), mp 187–189°C (Ref. [6] 186°C), 4,4'-(2-norboldidene)diphenol (diphenol N), mp 177–179°C (Ref. [7] 177–179°C), 4,4'-(1-cyclohexylidene)-di-(2,6-dibromophenol) (bromophenol C), mp 157–158°C (Ref. [8] 134.5–135.5°C), 4,4'-(2-norboldidene)-di-(2,6-dibromophenol) (bromodiphenol N), mp 180–181°C (Ref. [7] 180–181°C), 1,3-benzenedisulfonyl chloride (1,3-B), mp 61–62°C (Ref. [9] 62°C), 1-methyl-2,4-benzenedisulfonyl chloride (1-M-2,4-B), mp 51–52°C (lit. [10] 52.4–52.8°C), 1,3-dimethyl-4,6-benzenedisulfonyl chloride, (1,3-DM-4,6-B), mp 130°C, (Ref. [11] 130°C) 1,3,5-trimethyl-2,4-benzenedisulfonyl chloride (1,3,5-TM-2,4-B), mp 123–124°C (Ref. [12] 123.5–124°C).

## MEASUREMENT OF PROPERTIES

**Melting point.** Melting points were determined with the use of Boetius apparatus.

**Viscosity.** Reduced viscosity (dl/g) on 1% solution of polysulfonates in 1,1,2,2-tetrachloroethane was measured at 25°C with a Ubbelohde viscometer.

**Infrared (IR) spectra.** IR spectra were obtained with the use of UICAM SP-200 spectrophotometer.

**Thermogravimetric (TGA) analysis.** TGA analysis was obtained with the MOM derivatograph (Paulik, Paulik and Erdey, Budapest) at a programmed heating rate of 10°C/min.

**Molecular weight.** Molecular weight was determined by GPC with the use of (Waters Associates Type 200) chromatograph.

## SYNTHESIS OF POLYSULFONATES

A solution of (0.04 mole) sodium hydroxide in 50 cm<sup>3</sup> of water was added to a (0.02 mole) diphenol. To the obtained diphenol sodium salt of benzyltriethylammonium chloride (0.001 mole) was added. Then a solution (0.02 mole) of disulfonyl chloride in 50 cm<sup>3</sup> of a solvent (methylene chloride, ethylene chloride or benzene) was added dropwise at 25–27°C during 35–40 min and vigorous stirring. The mixture was stirred at 25–27°C for 1–3 h, then was added to 200 cm<sup>3</sup> of isopropanol. The product was washed with methanol (3 × 100 cm<sup>3</sup>), with water (3 × 100 cm<sup>3</sup>) and then with methanol (100 cm<sup>3</sup>). The polymer was dried under the reduced pressure at 80°C. The yield was 80–96%. The results of the elemental analysis are presented in Tables 1 and 2.

Table 1. Results of elemental analysis

Polysulfonates		Analysis					
Diphenol	Disulphonyl chloride	% C		% H		% S	
		Calcd	Found	Calcd	Found	Calcd	Found
Diphenol C	1,3-B	61.26	60.80	4.71	4.89	13.63	13.90
	1-M-2, 4-B	61.96	62.10	4.99	5.25	13.23	13.30
	1,3-DM-4,6-B	62.63	62.12	5.26	5.40	12.86	12.62
	1,3,5-TM-2,4-B	63.26	63.47	5.51	5.71	12.51	12.47
Diphenol N	1,3-B	62.22	61.85	4.60	4.91	13.29	13.50
	1-M-2,4-B	62.88	62.63	4.87	4.94	12.91	13.20
	1,3-DM-4,6-B	63.51	63.80	5.13	5.27	12.56	12.81
	1,3,5-TM-2,4B	64.10	63.90	5.38	5.53	12.22	12.40

## RESULTS AND DISCUSSION

## OPTIMIZATION OF INTERFACIAL POLYCONDENSATION CONDITIONS

Synthesis of the polysulfonates was carried out by interfacial polycondensation. Taking into account the yield and reduced viscosities (dl/g) of polysulfonates, the influence of the following parameters was studied: organic phase, reaction time, concentration and hydrochloride acceptor, catalyst, and aqueous to organic phase ratio. Methylene chloride, ethylene chloride, and benzene were used as the organic phase. It was found that the kind of organic phase and the reaction time influenced the value of the viscosity and the yield of polymers. The polycondensation reaction of all the polysulfonates was carried out at 25–27°C using stoichiometric quantities of reagents. Sodium hydroxide in the stoichio-

Table 2. Results of elemental analysis

Polysulfonates		Analysis					
Diphenol	Disulphonyl chloride	% C		% H		% Br	
		Calcd	Found	Calcd	Found	Calcd	Found
Bromo-diphenol C	1,3-B	36.66	36.92	2.31	2.40	40.66	40.31
	1-M-2,4-B	37.52	37.78	2.52	2.61	39.95	39.60
	1,3-DM-4,6-B	38.35	38.80	2.72	2.50	39.26	39.12
	1,3,5-TM-2,4-B	39.15	38.82	2.92	3.08	38.59	38.27
Bromo-diphenol N	1,3-B	37.62	37.30	2.27	2.50	40.05	39.83
	1-M-2,4-B	38.45	38.61	2.48	2.83	39.36	39.01
	1,3-DM-4,6-B	39.25	39.12	2.68	2.81	38.69	38.40
	1,3,5-TM-2,4-B	40.02	40.22	2.88	3.05	38.04	38.24

metric quantity was used as a hydrochloride acceptor and benzyltriethylammonium chloride (5% of weight in relation to diphenol) as a catalyst. Methylene chloride solvent of disulfonyl chloride was an organic phase. The reaction time was 1 to 3 h.

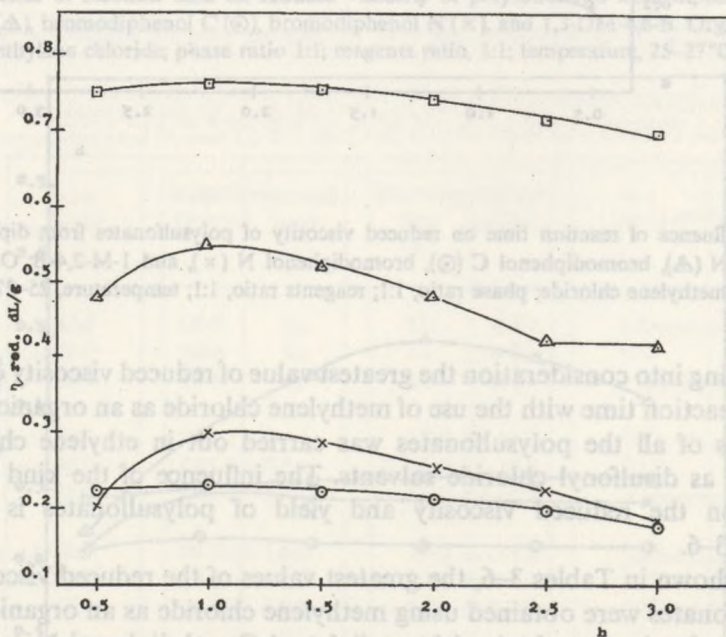


Fig. 1. Influence of reaction time reduced viscosity of polysulfonates from diphenol C (□) diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and 1,3-B. Organic phase, methylene chloride; phase ratio, 1:1; reagents ratio, 1:1; temperature, 25–27°C.

Figs. 1-4 show dependence of reduced viscosity on the reaction time. The optimal reaction time for all described polymers is not longer than 3 h. The reaction time appears to be dependent on both diphenol reactivity and hydrolysis rate of aromatic disulfonyl chlorides.

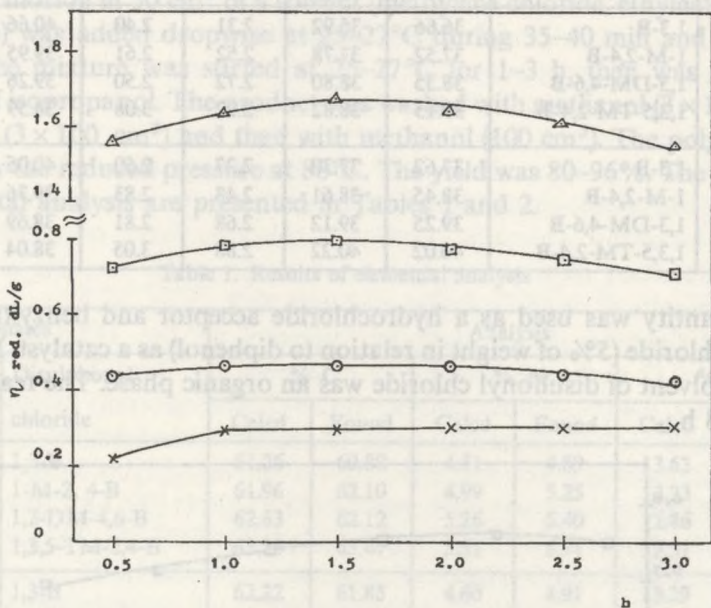


Fig. 2. Influence of reaction time on reduced viscosity of polysulfonates from diphenol C (□), diphenol N (△), bromodiphenol C (⊙), bromodiphenol N (×), and 1-M-2,4-B. Organic phase, methylene chloride; phase ratio, 1:1; reagents ratio, 1:1; temperature, 25-27°C

Taking into consideration the greatest value of reduced viscosity determined by the reaction time with the use of methylene chloride as an organic phase, the synthesis of all the polysulfonates was carried out in ethylene chloride and benzene as disulfonyl chloride solvents. The influence of the kind of organic phase on the reduced viscosity and yield of polysulfonates is shown in Tables 3-6.

As shown in Tables 3-6, the greatest values of the reduced viscosity of the polysulfonates were obtained using methylene chloride as an organic phase. In the case of polymers obtained from diphenol C and diphenol N, lower values were found for benzene and the lowest for ethylene chloride. For polymers derived from bromodiphenol C and bromodiphenol N, lower values were obtained for ethylene chloride and the lowest ones for benzene. The influence of the kind of organic phase on the reaction yield was not observed.

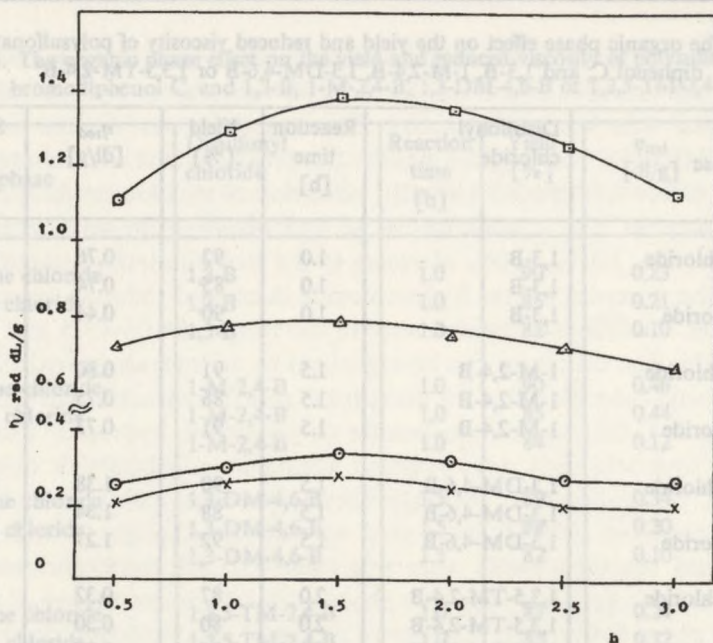


Fig. 3. Influence of reaction time on reduced viscosity of polysulfonates from diphenol C (□), diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and 1,3-DM-4,6-B. Organic phase, methylene chloride; phase ratio 1:1; reagents ratio, 1:1; temperature, 25–27°C

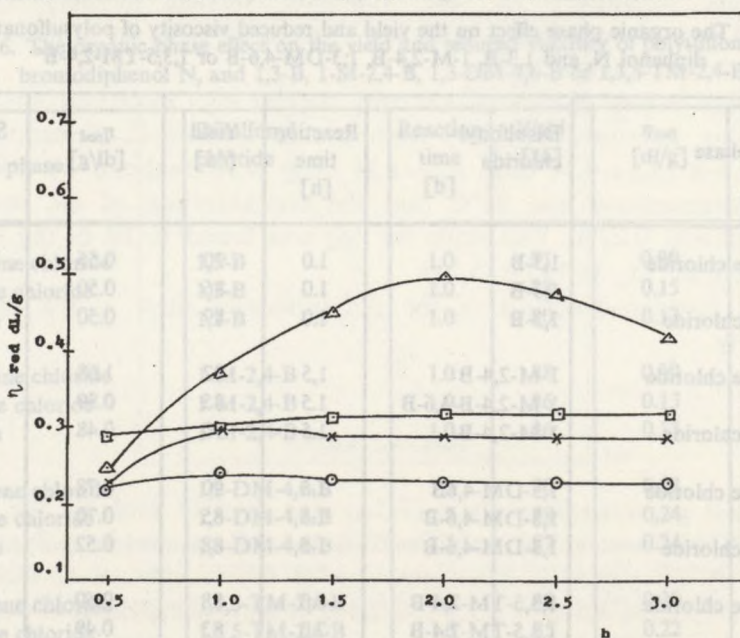


Fig. 4. Influence of reaction time on reduced viscosity of polysulfonates from diphenol C (□), diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and 1,3,5-TM-2,4-B. Organic phase, methylene chloride; phase ratio, 1:1; reagents ratio, 1:1; temperature, 25–27°C

Table 3. The organic phase effect on the yield and reduced viscosity of polysulfonates from diphenol C, and 1,3-B, 1-M-2,4-B, 1,3-DM-4,6-B or 1,3,5-TM-2,4-B<sup>a</sup>

Organic phase	Disulfonyl chloride	Reaction time [h]	Yield [%]	$\eta_{red}$ [dl/g]	Softening range [°C]
Methylene chloride	1,3-B	1.0	92	0.76	180–230
Benzene	1,3-B	1.0	85	0.74	160–220
Ethylene chloride	1,3-B	1.0	90	0.44	180–250
Methylene chloride	1-M-2,4-B	1.5	91	0.80	170–245
Benzene	1-M-2,4-B	1.5	86	0.75	220–265
Ethylene chloride	1-M-2,4-B	1.5	91	0.73	170–250
Methylene chloride	1,3-DM-4,6-B	1.5	90	1.38	250–280
Benzene	1,3-DM-4,6-B	1.5	88	1.34	220–250
Ethylene chloride	1,3-DM-4,6-B	1.5	92	1.27	280–310
Methylene chloride	1,3,5-TM-2,4-B	2.0	87	0.32	250–305
Benzene	1,3,5-TM-2,4-B	2.0	80	0.30	180–240
Ethylene chloride	1,3,5-TM-2,4-B	2.0	85	0.27	250–300

<sup>a</sup> Conditions of the reaction: phase ratio, 1:1; reagents ratio, 1:1; temperature, 25–27°C

Table 4. The organic phase effect on the yield and reduced viscosity of polysulfonates from diphenol N, and 1,3-B, 1-M-2,4-B, 1,3-DM-4,6-B or 1,3,5-TM-2,4-B<sup>a</sup>

Organic phase	Disulfonyl chloride	Reaction time [h]	Yield [%]	$\eta_{red}$ [dl/g]	Softening range [°C]
Methylene chloride	1,3-B	1.0	90	0.55	200–270
Benzene	1,3-B	1.0	86	0.50	180–250
Ethylene chloride	1,3-B	1.0	89	0.50	190–220
Methylene chloride	1-M-2,4-B	1,5	92	1.68	220–260
Benzene	1-M-2,4-B-4,6-B	1.5	85	0.89	230–280
Ethylene chloride	1-M-2,4-B	1.5	90	0.48	230–290
Methylene chloride	1,3-DM-4,6B	1.5	90	0.78	230–260
Benzene	1,3-DM-4,6-B	1.5	85	0.70	215–250
Ethylene chloride	1,3-DM-4,6-B	1.5	88	0.52	250–280
Methylene chloride	1,3,5-TM-2,4-B	2.0	88	0.50	260–310
Benzene	1,3,5-TM-2,4-B	2.0	83	0.49	230–270
Ethylene chloride	1,3,5-TM-2,4-B	2.0	84	0.27	200–250

<sup>a</sup> Conditions of the reaction: phase ratio, 1:1; reagents ratio, 1:1; temperature, 25–27°C



Table 5. The organic phase effect on the yield and reduced viscosity of polysulfonates from bromodiphenol C, and 1,3-B, 1-M-2,4-B, 1,3-DM-4,6-B or 1,3,5-TM-2,4-B<sup>a</sup>

Organic phase	Disulfonyl chloride	Reaction time [h]	Yield [%]	$\eta_{red}$ [dl/g]	Softening range [°C]
Methylene chloride	1,3-B	1.0	90	0.23	260–295
Ethylene chloride	1,3-B	1.0	85	0.21	230–280
Benzene	1,3-B	1.0	82	0.10	215–270
Methylene chloride	1-M-2,4-B	1.0	90	0.46	280–305
Ethylene chloride	1-M-2,4-B	1.0	85	0.44	210–270
Benzene	1-M-2,4-B	1.0	84	0.12	250–280
Methylene chloride	1,3-DM-4,6-B	1.5	89	0.34	285–310
Ethylene chloride	1,3-DM-4,6-B	1.5	88	0.20	235–285
Benzene	1,3-DM-4,6-B	1.5	82	0.10	256–280
Methylene chloride	1,3,5-TM-2,4-B	1.0	87	0.24	260–310
Ethylene chloride	1,3,5-TM-2,4-B	1.0	85	0.22	270–310
Benzene	1,3,5-TM-2,4-B	1.0	83	0.10	180–270

<sup>a</sup> Conditions of the reaction: phase ratio, 1:1; reagents ratio, 1:1; temperature, 25–27°CTable 6. The organic phase effect on the yield and reduced viscosity of polysulfonates from bromodiphenol N, and 1,3-B, 1-M-2,4-B, 1,3-DM-4,6-B or 1,3,5-TM-2,4-B<sup>a</sup>

Organic phase	Disulfonyl chloride	Reaction time [h]	Yield [%]	$\eta_{red}$ [dl/g]	Softening range [°C]
Methylene chloride	1,3-B	1.0	91	0.30	270–300
Ethylene chloride	1,3-B	1.0	88	0.15	240–270
Benzene	1,3-B	1.0	80	0.13	220–250
Methylene chloride	1-M-2,4-B	1.0	88	0.30	270–310
Ethylene chloride	1-M-2,4-B	1.0	86	0.13	240–285
Benzene	1-M-2,4-B	1.0	86	0.13	260–295
Methylene chloride	1,3-DM-4,6-B	1.5	90	0.28	250–280
Ethylene chloride	1,3-DM-4,6-B	1.5	88	0.24	260–285
Benzene	1,3-DM-4,6-B	1.5	87	0.24	270–290
Methylene chloride	1,3,5-TM-2,4-B	1.0	89	0.30	280–305
Ethylene chloride	1,3,5-TM-2,4-B	1.0	85	0.22	240–280
Benzene	1,3,5-TM-2,4-B	1.0	82	0.20	230–260

<sup>a</sup> Condition of the reaction: phase ratio, 1:1; reagents ratio, 1:1; temperature, 25–27°C

The influence of the concentration of sodium hydroxide as a hydrochloride acceptor in the aqueous phase on the reduced viscosity and polycondensation reaction yield was also determined. The reaction was carried out using methylene chloride as an organic phase. The reaction time was determined by the greatest value of reduced viscosity obtained at stoichiometric quantity of sodium hydroxide. The concentration of hydrochloride in an organic phase varied using 50%, 100%, 150% of excess to the stoichiometric quantity. It was found that the acceptor excess hydrochloride decreased reduced viscosity and reaction yield. Reduced viscosities were in the range of 0.05–0.75 and reaction yields 50–60%. The decreases can be explained by an increase in hydrolysis rate of aryldisulfonyl chloride when the acceptor excess of hydrochloride was used. It should be added, that sodium carbonate or potassium hydroxide used as the acceptor of hydrochloride gave reduced viscosities of about 0.9 dl/g. In the synthesis of polysulfonates, benzyltriethylammonium chloride and benzyltrimethylammonium chloride were used as catalysts, changes in both reduced viscosities and reaction yields were not observed. All the experiments were carried out at the aqueous to organic phase ratio 1:1 (concentration of diphenol on aqueous phase 0.4 mole/l). Change of diphenol concentration decreased the values of reduced viscosity and reaction yield.

Elemental analysis and infrared spectra were obtained for all the polymers. Adsorptions attributed to the sulfonate linkage ( $-\text{SO}_2-\text{O}-$ ) at  $1,200\text{--}1,145\text{ cm}^{-1}$  and  $1,420\text{--}1,330\text{ cm}^{-1}$  were valuable in establishing the presence of these groups.

The high values of reduced viscosity suggest high molecular weights. To confirm this, polymers obtained from bromodiphenol C, diphenol C and 1,3-DM-4,6-B ( $\eta_{red}=0.34\text{ dl/g}$ ,  $\eta_{red}=1.38\text{ dl/g}$ ) were analyzed by GPC. The analysis temperature was  $25^\circ\text{C}$  and the concentration of the sample in tetrahydrofuran 0.25%. The value for  $\bar{M}_n$  was found to be of the order of 3,200–6,000, for  $\bar{M}_w$  19,500–115,200.

X-ray powder diagrams of the polysulfonates show a low degree of crystallinity.

#### THERMAL ANALYSIS

Thermal gravimetric analysis (TGA) was used to evaluate the thermal stability polysulfonates. Fig. 5 shows TGA and DTA curves for polysulfonates obtained by interfacial polycondensation of bromodiphenol C with 1,3-B, 1-M-2,4-B, 1,3-DM-4,6-B or 1,3,5-TM-2,4-B. A fairly sharp onset of weight loss is noted around  $290\text{--}300^\circ\text{C}$ . Since the majority of the polymers show loss of weight in the  $290\text{--}340^\circ\text{C}$  region, the upper limits of stability appear to be governed by the stability of the sulfonate linkage. The polymer melts and

decomposes with the evolution of sulfur dioxide, indicating that the sulfonate linkage is the weak spot in the chain. The polymers obtained in the reaction of diphenol C and diphenol N with 1,3-B, 1-M-2,4-B, 1,3-DM-4,6-B or 1,3,5-TM-2,4-B were found to show higher thermal stability than polymers of bromodiphenol C and bromodiphenol N. The results of thermal stability of polysulfonates are presented in Table 7.

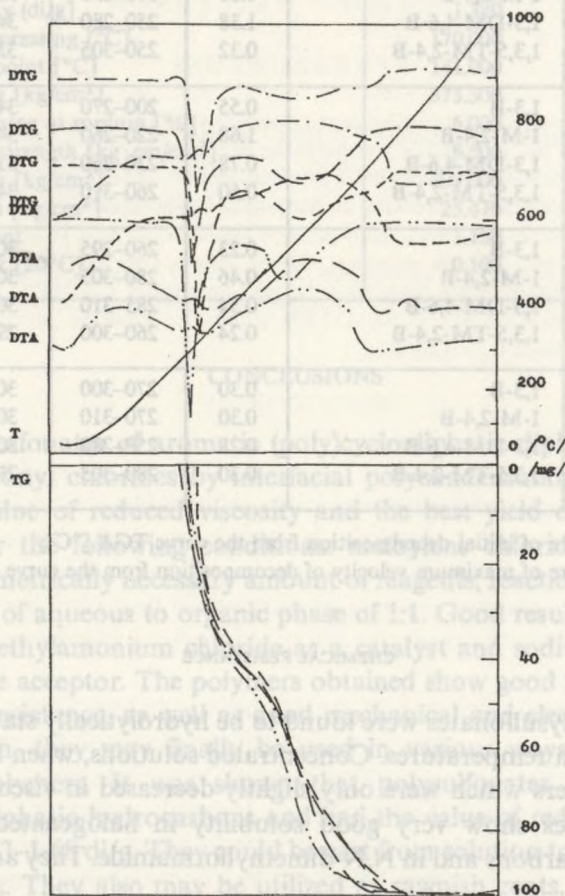


Fig. 5. TGA and DTA of polysulfonates from bromodiphenol C, 1,3-B (—), 1-M-2,4-B (----), 1,3-DM-4,6-B (-.-.-), and 1,3,5-TM-2,4-B (.....). Heating time in air, 100 min; heating rate, 10°C/min; amount of polysulfonates 100 mg; measured in relation to  $Al_2O_3$ .

Table 7. Thermal properties of polysulfonates

Polysulfonates		$\eta_{red}$ [dl/g]	Softening range [°C]	Thermal analysis <sup>a</sup>	
Diphenol	Disulfonyl chloride			$T_1$ [°C]	$T_2$ [°C]
Diphenol C	1,3-B	0.76	180–230	320	380
	1-M-2,4-B	0.80	170–295	320	390
	1,3-DM-4,6-B	1.38	250–280	340	400
	1,3,5-TM-2,4-B	0.32	250–305	320	360
Diphenol N	1,3-B	0.55	200–270	340	400
	1-M-2,4-B	1.68	220–260	340	390
	1,3-DM-4,6-B	0.78	230–260	310	360
	1,3,5-TM-2,4-B	0.50	260–310	340	380
Bromodiphenol C	1,3-B	0.23	260–295	300	340
	1-M-2,4-B	0.46	280–305	300	340
	1,3-DM-4,6-B	0.34	285–310	300	340
	1,3,5-TM-2,4-B	0.24	260–300	290	330
Bromodiphenol N	1,3-B	0.30	270–300	300	340
	1-M-2,4-B	0.30	270–310	300	340
	1,3-DM-4,6-B	0.28	250–280	300	340
	1,3,5-TM-2,4-B	0.30	280–305	290	330

<sup>a</sup>  $T_1$  = temperature of initial decomposition from the curve TGA [°C];

$T_2$  = temperature of maximum velocity of decomposition from the curve TGA [°C].

#### CHEMICAL RESISTANCE

All of the polysulfonates were found to be hydrolytically stable to both acid and base at room temperatures. Concentrated solutions, when heated for 24 h, produced polymers which were only slightly decreased in viscosity.

Polysulfonates show very good solubility in halogenated aliphatic and aromatic hydrocarbons and in N,N-dimethylformamide. They are not soluble in alcohols.

#### MECHANICAL PROPERTIES

Mechanical and electrical properties of some polysulfonates obtained by polycondensation of diphenol C and bromodiphenol C with 1,3-DM-4,6-B were also examined. Polymers were pressed in a steel mould under pressure of 200 kg/cm<sup>2</sup> at elevated temperature. The obtained results are shown in Table 8.

Table 8. Temperature of pressing: mechanical and electrical properties of polysulfonates

Property	1,3-DM-4,6-B	
	Diphenol C	Bromodiphenol C
Reduced viscosity (dl/g)	1.380	0.340
Temperature of pressing [°C]	170.000	195.000
Vicat softening point [°C]	141.000	158.000
Rupture strength [kg/cm <sup>2</sup> ]	375.500	—
Relative lengthening at rupture [%]	6.000	—
Dynstat impact strength [kg·cm/cm <sup>2</sup> ]	6.500	—
Bending strength [kg/cm <sup>2</sup> ]	409.000	—
Brinell hardness [kg/cm <sup>2</sup> ]	25.470	23.150
Dielectric constant	1.150	2.040
tan $\delta$ at 170 kHz [20°C]	0.100	0.021

### CONCLUSIONS

New polysulfonates of aromatic (poly)cycloaliphatic diphenols with some aromatic disulfonyl chlorides by interfacial polycondensation were obtained. The highest value of reduced viscosity and the best yield of polymers were achieved under the following conditions: methylene chloride as an organic phase, stoichiometrically necessary amount of reagents, reaction temperature at 25–27°C, ratio of aqueous to organic phase of 1:1. Good results were obtained using benzyltriethylammonium chloride as a catalyst and sodium hydroxide as a hydrochloride acceptor. The polymers obtained show good thermal, physical and chemical resistance, as well as good mechanical and electrical properties. For this reason, they may finally be used in various ways as modifiers of commercial polymers. It was shown that polysulfonates were soluble in halogenated aliphatic hydrocarbons and had the value of reduced viscosity in the range of 0.23–1.68 dl/g. They could be cast from solution to give clear tough films and fibers. They also may be utilized as rawnish coats, because of their suitable value of reduced viscosity.

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## STRESZCZENIE

Nowe aromatyczno(poly)cycloalifatyczne polisulfoniany otrzymano przez polikondensację na granicy rozdziału faz w układzie dwufazowym złożonym z fazy organicznej i fazy wodnej 4,4'-(1-cykloheksylideno)difenolu i 4,4'-(2-norbolideno)difenolu z *m*-benzenodwusulfochlorkiem i jego metylowymi homologami w obecności wodorotlenków lub węglanów metali alkalicznych jako akceptorów chlorowodoru i czwartorzędowych soli amonowych jako katalizatora. Rozpuszczalnikami organicznymi były chlorek metylenu, chlorek etylenu i benzen. Otrzymane polisulfoniany mają niski stopień krystaliczności, topią się w zakresie temperatur 170–310°C, masa cząsteczkowa  $\bar{M}_n$  w granicach 3200–6000  $\bar{M}_w$  19 500–115 200, stabilność termiczna powyżej 290°C, lepkość zredukowana w granicach 0,23–1,68 dl/g.