

Linear Polysulfonates. I. Products of 4,4'-(1-Cyclohexylidene)Diphenol and 4,4'-(2-Norboldiene)Diphenol with Some Aromatic Disulfonyl Chlorides

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Synopsis

Aromatic (poly)cycloaliphatic polysulfonates of high molecular weight can be easily obtained by interfacial polycondensation of aromatic (poly)cycloaliphatic diphenols with aromatic disulfonyl chlorides. The polysulfonates were found to have a low degree of crystallinity, softening ranges in the region 180–310°C and molecular weights in the region: \bar{M}_n 3190–4420, and \bar{M}_w 19900–83370, thermal stability to above 300°C, and reduced viscosities in the range 0.2–1.00 dL/g.

INTRODUCTION

It has been known from the chemical literature that aromatic polysulfonates of good physical, chemical, and thermal properties are obtained by interfacial polycondensation of aromatic diphenols with aromatic disulfonyl chlorides in the presence of quarternary ammonium salts as a catalyst.

The first synthesis of aromatic polysulfonates was carried out by Conix¹ from 4,4'-diphenyletherdisulfonyl chloride in methylene chloride and sodium salt of dihydroxydiphenylmethane and in the presence of benzyltriethylammonium chloride as a catalyst.

Distler and Göelz,² using 4,4'-dihydroxydiphenylsulfone and bisphenol-A and 1,3-propanedisulfonyl chloride and 1,4-cyclohexane disulfonyl chloride, obtained thermoplastic resistant to saponification and melting without decomposition of polysulfonates.

Studies of synthesis and properties of polysulfonates were carried out by Thomson and Ehlers,³ who obtained some new aromatic polysulfonates. Aromatic radicals of these polysulfonates derived from diphenols and disulfonyl chlorides were represented by, 1,3-benzene, 4,4'-diphenyl, 4,4'-diphenylether, 4,4'-diphenylmethane, and 4,4'-diphenyl sulfone. Structures, thermal stabilities, and molecular weights were also found.

Polysulfonates of good chemical resistance were obtained by interfacial polycondensation of bisphenol-A, 1,1-di(4-hydroxyphenyl)-ethane, *m*-benzenedisulfonyl chloride, and 1,5-naphthalene-disulfonyl chloride in the presence of alkalis as hydrogen chloride acceptors.⁴

Aromatic polysulfonates of good physical, chemical, and electrical properties were obtained⁵ by the reaction of bisphenol-A with the mixture of

methylbenzenedisulfonyl chlorides or with the mixture of *m*-xylene-4,6 and diphenylether-4,4'-disulfonyl chlorides.

It is known,^{6,7} that polysulfonates of good stability, plastics, and adhesive properties can be prepared by interfacial polycondensation of bisphenol-A or 2,2-bis(3,5-dichloro-4-hydroxyphenyl)-propane with benzenedisulfonyl chloride and methylbenzenedisulfonyl chloride in the presence of benzyltrimethylammonium chloride.

Polysulfonates obtained by interfacial polycondensation of bisphenol-A, hydroquinone with *m*-benzenedisulfonyl chloride in the presence of benzyltrimethylammonium chloride and sodium lauryl sulfate as a catalyst, were characterized by Fontan Yanes and co-workers.⁸

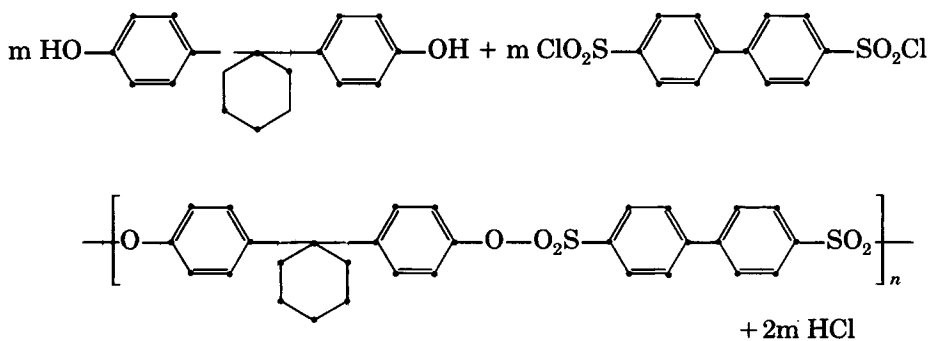
It was stated that films and fibers forming polysulfonates can be obtained from aromatic diphenols and diphenyletherdisulfonyl chloride.⁹ Copolymers with good properties, utilized as protecting coats were obtained from bisphenol-A and 2,4-toluenedisulfonyl chloride in the presence of benzyltrimethylammonium chloride as a catalyst.¹⁰

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 film and fiber formation from solutions. Conventional techniques of thermoplastics treatment such as: extrusion, injection moulding, and pressing are also possible.

In searching for new polysulfonates which might also have good physical, chemical, and thermal properties, the preparation and characterization of a series of new aromatic(poly)cycloaliphatic polysulfonates were studied. It was found that polysulfonates of high molecular weight would be easily obtained by interfacial polycondensation of aromatic(poly)cycloaliphatic diphenols with aromatic disulfonyl chlorides.

4,4'-(1-cyclohexylidene)diphenol, 4,4'-(2-norbolidene)diphenol, 4,4'-(1-cyclohexylidene)-di-(2,6-dibromophenol), and 4,4'-/2-norbolideno-di-(2,6-dibromophenol) were used as diphenols. Diphenyl 4,4'-, diphenyl ether 4,4'-, diphenyl thioether 4,4'-, and diphenyl methane 4,4'-disulfonyl chloride were used as aromatic disulfonyl chlorides.

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



Some of the above-mentioned diphenols were used in the synthesis of new polycarbonates and polyesters¹¹ of good physical properties. The polymers showed good solubility in low-boiling solvents, high modulus of elasticity, and were especially useful for fabrication of products with very good electrical properties and they very resistant at elevated temperatures.

Taking into account these conclusions, it seemed suitable to prepare some new polysulfonates using the above-mentioned reagents and to characterize their properties.

EXPERIMENTAL

Reagents

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

The following aromatic disulfonyl chlorides were obtained by direct chlorosulfonation of adequate hydrocarbons or in the reaction of potassium or sodium salts of arylodisulfonic acids with PCl_5 or with PCl_5 in the presence of POCl_3 .

4,4'-(1-cyclohexylidene)diphenol (diphenol-C) mp 187–189°C (lit.¹² 186°C), 4,4'-(2-norboldiene)diphenol (diphenol-N), mp 177–179°C (lit.¹¹ 177–179°C), 4,4'-(1-cyclohexylidene)-di-(2,6-dibromophenol) (Bromodiphenol-C), mp 157–158°C (lit.¹³ 134.5–135.5°C), 4,4'-(2-norboldiene)-di-(2,6-dibromophenol) (bromodiphenol-N), mp 180–181°C (lit.¹¹ 180–181°C), 4,4'-diphenyldisulfonyl chloride (DPh), mp 210–211°C (lit.¹⁴ 203°C), 4,4'-diphenyletherdisulfonyl chloride (DPhE), mp 126–128°C (lit.¹⁵ 128–129°C), 4,4'-diphenylthioetherdisulfonyl chloride (DPhTE), mp 157–158°C (lit.¹⁶ 155–156°C) 4,4'-diphenylmethanedisulfonyl chloride (DPhM), mp 126–128°C (lit.¹⁷ 124°C).

Measurement of Properties

Melting Point. Melting points were determined with the use of Böetius 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 UNICAM SP-200 spectrophotometer.

Thermogravimetric (TGA) Analysis. TGA analysis was obtained with the use of 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 mol) sodium hydroxide in 75 cm³ of water was added to a (0.02 mole) diphenol. To the obtained diphenol sodium salt of benzyltriethylammonium chloride (0.001 mol) was added. Then a solution of (0.02 mol) disulfonyl chloride in 75 cm³ of a solvent (methylene chloride, ethylene chloride, or benzene) was added dropwise at 25–27°C during 35–40 min at

TABLE I
Results of Elemental Analysis

Polysulfonates		Analysis					
Diphenol	Disulfonyl chloride	% C		% H		% S	
		Calcd	Found	Calcd	Found	Calcd	Found
Diphenol C	DPh	65.91	65.66	4.81	4.97	11.73	11.90
	DPhE	64.04	63.80	4.66	4.83	11.37	11.30
	DPhTE	62.26	62.40	4.53	4.78	16.62	16.24
	DPhM	66.40	66.80	5.03	5.40	11.43	11.51
Diphenol N	DPh	66.64	66.20	4.49	4.97	11.48	11.85
	DPhE	64.79	65.00	4.57	4.20	11.16	11.40
	DPhTE	63.02	62.75	4.44	4.49	16.28	16.58
	DPhM	67.11	66.80	4.92	4.57	11.19	11.45

TABLE II
Results of Elemental Analysis

Polysulfonates		Analysis					
Bromodiphenol	Disulfonyl chloride	% C		% C		% Br	
		Calcd	Found	Calcd	Found	Calcd	Found
Bromodiphenol C	DPh	41.78	41.30	2.57	2.96	37.07	36.52
	DPhE	41.02	41.06	2.52	2.71	36.36	36.13
	DPhTE	40.28	39.90	2.48	2.71	35.74	35.40
	DPhM	42.48	42.00	2.76	2.96	36.51	35.98
Bromodiphenol N	DPh	41.58	42.15	2.54	2.85	36.56	36.00
	DPhE	41.82	41.30	2.49	2.60	35.90	35.63
	DPhTE	41.08	39.71	2.45	2.80	35.26	34.84
	DPhM	43.26	42.81	2.72	2.92	35.98	35.48

vigorous stirring. The mixture was stirred at 25–27 °C for 1–3 h and then the whole was added to 200 cm³ of isopropanol. The product was washed with methanol (3 × 100 cm³), with water (3 × 100 cm³) and then with methanol (100 cm³). The polymer was dried under reduced pressure at 80 °C. The yield was 80–96%. Results of the elemental analysis are presented in Tables I and II.

RESULTS AND DISCUSSION

Optimization of Interfacial Polycondensation Conditions

Synthesis of the polysulfonates was carried out by interfacial polycondensation. Taking into account yields 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 influence the value of the viscosity and the yield of polymers. The polycondensation reaction of all the polysulfonates was

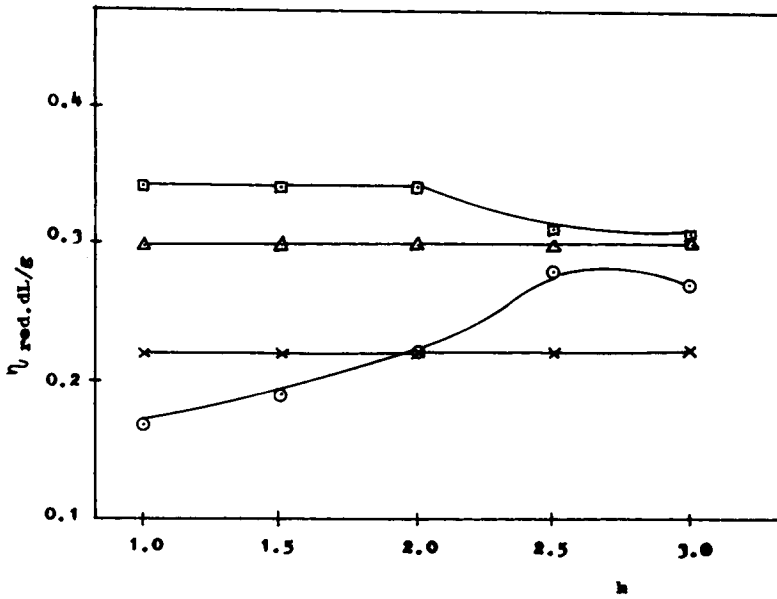


Fig. 1. Influence of reaction time on reduced viscosity of Polysulfonates from diphenol C (□), diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and DPh. Organic phase, methylene chloride; phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature 25–27° C.

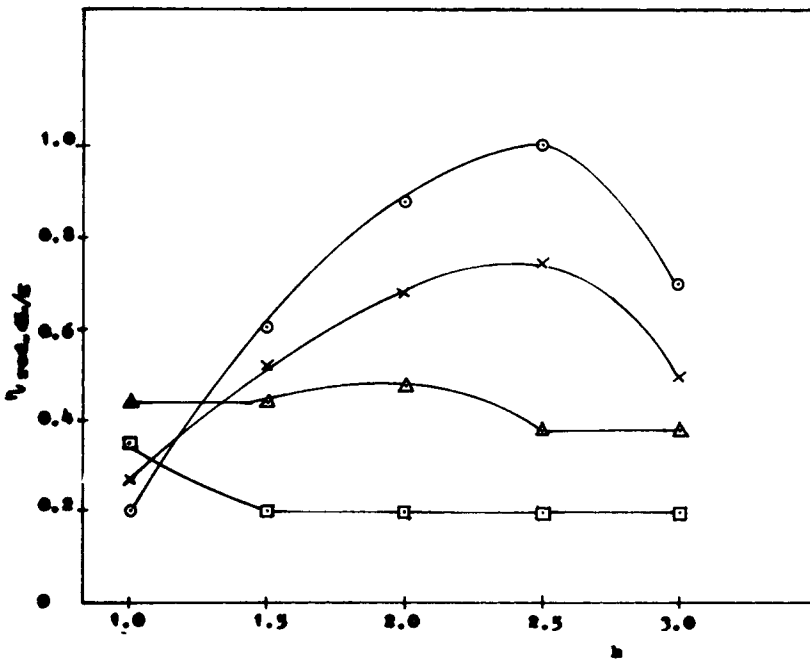


Fig. 2. Influence of reaction time on reduced viscosity of Polysulfonates from diphenol C (□), diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and DPhE. Organic phase, methylene chloride; phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27° C.

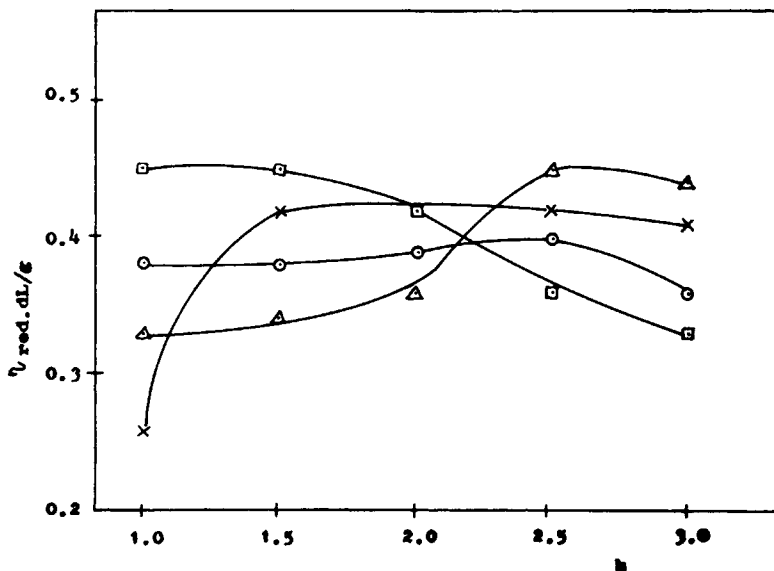


Fig. 3. Influence of reaction time on reduced viscosity of Polysulfonates from diphenol C (□), diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and DPhTE. Organic phase, methylene chloride; phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27 °C.

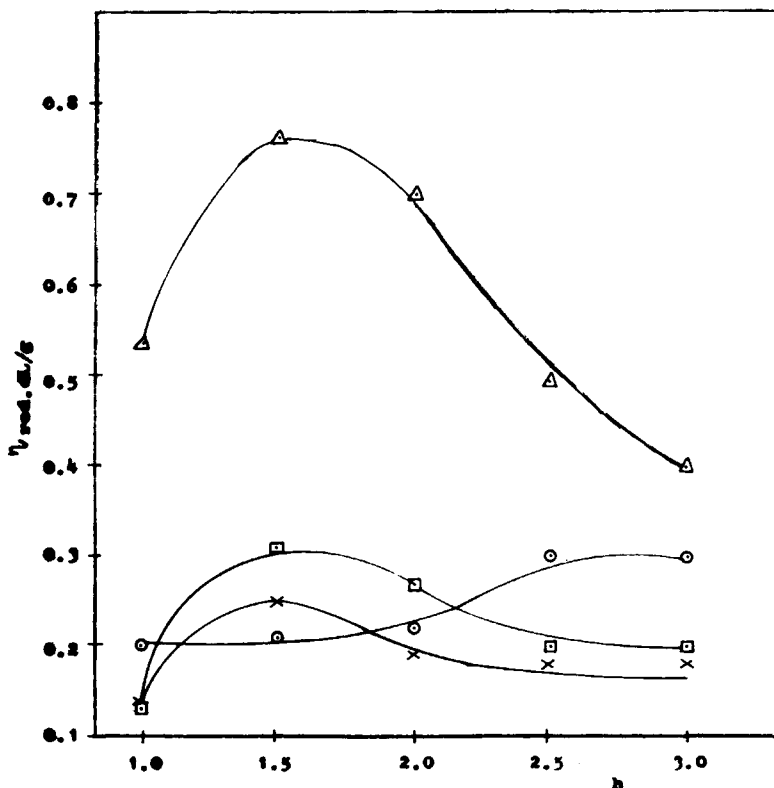


Fig. 4. Influence of reaction time on reduced viscosity of Polysulfonates from diphenol C (□), diphenol N (Δ), bromodiphenol C (○), bromodiphenol N (×), and DPhM. Organic phase, methylene chloride; phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27 °C.

TABLE III
The Organic Phase Effect on the Yield and Reduced Viscosity of Polysulfonates
from Diphenol C, and DPh, DPhTE or DPhM^a

Organic phase	Disulfonyl chloride	Reaction time (h)	Yield (%)	η_{red} (dL/g)	Softening range (°C)
Methylene chloride	DPh	1	91	0.34	260–310
Benzene	DPh	1	80	0.34	250–260
Ethylene chloride	DPh	1	90	0.30	270–310
Methylene chloride	DPhE	1	91	0.35	190–240
Benzene	DPhE	1	85	0.32	285–310
Ethylene chloride	DPhE	1	93	0.23	265–300
Methylene chloride	DPhTE	1	96	0.45	255–295
Benzene	DPhTE	1	80	0.34	250–300
Ethylene chloride	DPhTE	1	85	0.30	260–300
Methylene chloride	DPhM	1.5	90	0.31	260–305
Benzene	DPhM	1.5	85	0.25	260–300
Ethylene chloride	DPhM	1.5	90	0.25	250–300

^a Conditions of the reaction: phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27 °C.

TABLE IV
The Organic Phase Effect on the Yield and Reduced Viscosity of Polysulfonates
from Diphenol N and DPh, DPhE, DPhTE, or DPhM^a

Organic phase	Disulfonyl chloride	Reaction time (h)	Yield (%)	η_{red} (dL/g)	Softening range (°C)
Methylene chloride	DPh	1	90	0.30	280–310
Benzene	DPh	1	92	0.28	250–310
Ethylene chloride	DPh	1	95	0.25	245–300
Methylene chloride	DPhE	2	90	0.48	270–310
Benzene	DPhE	2	95	0.40	270–310
Ethylene chloride	DPhE	2	95	0.28	270–305
Methylene chloride	DPhTE	2.5	95	0.45	290–300
Benzene	DPhTE	2.5	90	0.34	260–300
Ethylene chloride	DPhTE	2.5	90	0.27	280–305
Methylene chloride	DPhM	1.5	91	0.76	275–290
Benzene	DPhM	1.5	95	0.65	280–305
Ethylene chloride	DPhM	1.5	90	0.34	260–300

^a Conditions of the reaction: phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27 °C.

carried out at 25–27 °C using stoichiometric quantities of reagents. Sodium hydroxide in the stoichiometric 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.

Figures 1–4 show dependence of reduced viscosity on 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 aromaticdisulfonyl chlorides.

Taking into consideration the greatest value of reduced viscosity determined by the reaction time with the use of methylene chloride as an

TABLE V
The Organic Phase Effect on the Yield and Reduced Viscosity of Polysulfonates
from Bromodiphenol C and DPh, DPhE, DPhTE, or DPhM^a

Organic phase	Disulfonyl chloride	Reaction time (h)	Yield (%)	η_{red} (dL/g)	Softening range (° C)
Methylene chloride	DPh	2.5	91	0.28	280–305
Ethylene chloride	DPh	2.5	86	0.25	255–295
Benzene	DPh	2.5	80	0.20	240–270
Methylene chloride	DPhE	2.5	95	1.00	280–295
Ethylene chloride	DPhE	2.5	95	0.30	285–295
Benzene	DPhE	2.5	85	0.27	260–305
Methylene chloride	DPhTE	2.5	80	0.40	270–290
Ethylene chloride	DPhTE	2.5	85	0.32	270–290
Benzene	DPhTE	2.5	80	0.30	280–295
Methylene chloride	DPhM	2.5	85	0.30	250–300
Ethylene chloride	DPhM	2.5	90	0.20	260–300
Benzene	DPhM	2.5	81	0.20	180–240

^a Conditions of the reaction: phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27° C.

TABLE VI
The Organic Phase Effect on the Yield and Reduced Viscosity of Polysulfonates
from Bromodiphenol N, and DPh, DPhE, DPhTE, or DPhM^a

Organic phase	Disulfonyl chloride	Reaction time (h)	Yield (%)	η_{red} (dL/g)	Softening range (° C)
Methylene chloride	DPh	1.5	90	0.22	270–300
Ethylene chloride	DPh	1.5	90	0.17	240–280
Benzene	DPh	1.5	90	0.16	260–300
Methylene chloride	DPhE	2.5	96	0.74	280–295
Ethylene chloride	DPhE	2.5	95	0.15	270–290
Benzene	DPhE	2.5	95	0.15	260–300
Methylene chloride	DPhTE	1.5	96	0.42	260–290
Ethylene chloride	DPhTE	1.5	90	0.14	265–280
Benzene	DPhTE	1.5	90	0.14	270–290
Methylene chloride	DPhM	1.5	92	0.25	255–295
Ethylene chloride	DPhM	1.5	95	0.21	260–300
Benzene	DPhM	1.5	91	0.14	200–250

^a Conditions of the reaction: phase ratio, 1 : 1; reagents ratio, 1 : 1; temperature, 25–27° C.

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 III–VI.

As Tables III–VI show, the greatest values of the reduced viscosity for all 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 ones 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.

The influence of the concentration of sodium hydroxide as hydrochloride acceptor in 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 was varied using 50, 100, 150% of excess to the stoichiometric quantity. It was found that the acceptor excess of hydrochloride decreases reduced viscosity and reaction yield. Reduced viscosities were in the range of 0.09–0.18 dL/g and reaction yields 50–65%. The decreases can be explained by an increase in hydrolysis rate of arylodisulfonyl chloride when acceptor excess of hydrochloride was used. It should be added, that sodium carbonate or potassium hydroxide used as acceptor of hydrochloride gave reduced viscosities of about 0.2 dL/g. In the synthesis of polysulfonates, benzyltrimethylammonium chloride and benzyltriethylammonium 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 in aqueous phase 0.26 mole/L). Changes of diphenol concentration decrease 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 1200–1145 cm^{-1} and 1420–1330 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 and DPhE ($\eta_{\text{red}} = 0.35$ dL/g, $\eta_{\text{red}} = 1.00$ dL/g) were analyzed by GPC. The analysis temperature was 25°C and the concentration of the sample in tetrahydrofuran 0.25%. The value for \bar{M}_n was found to be on the order of 3190–4420, for \bar{M}_w 19900–83370.

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 of polysulfonates. Figure 5 shows TGA and DTA curves for polysulfonates obtained by interfacial polycondensation of bromodiphenol C with DPh, DPhE, DPhTE or DPhM. A fairly sharp onset of weight loss is noted around 300–310°C. Since the majority of the polymers show loss of weight in the 295–360°C region, the upper limits of stability appear to be governed by the stability of the sulfonate linkage. The polymer melts decompose 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 DPh, DPhE, DPhTE, or DPhM were found to show higher thermal stability than polymers of bromodiphenol C and bromodiphenol N. Results of thermal stability of polysulfonates are presented in Table VII.

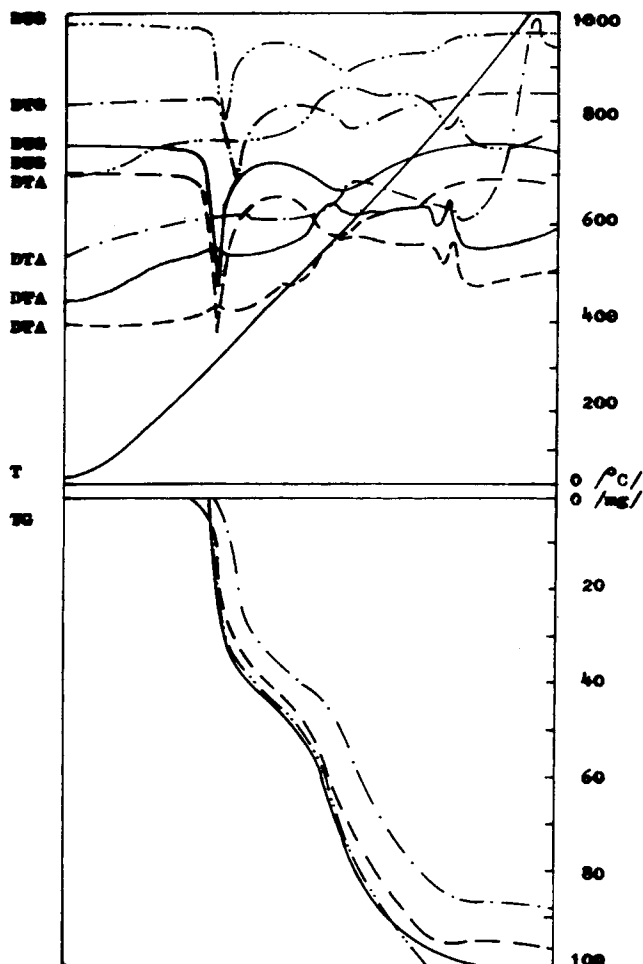


Fig. 5. TGA and DTA of polysulfonates from bromodiphenol C, DPh (—), DPhE (---), DPhTE (- · -), and DPhM (- · · -). Heating time in air, 100 min; heating rate, 10° C/min; amount of polysulfonates 100 mg; measured relative to Al₂O₃.

Chemical Resistance

All of the polysulfonates were found to be hydrolytically stable to both dissolved and concentrated mineral acids and alkaline solutions at room temperatures.

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 DPhE were also examined. Polymers were pressed in a steel mold under pressure of 200 kg/cm²

TABLE VII
 Thermal Properties of Polysulfonates

Polysulfonates		η_{red} (dL/g)	Softening range (°C)	Thermal analysis ^a	
Diphenol	Disulfonyl chloride			T ₁ (°C)	T ₂ (°C)
Diphenol C	DPh	0.34	260–310	350	380
	DPhE	0.35	190–240	320	380
	DPhTE	0.45	260–300	310	380
	DPhM	0.31	260–305	360	390
Diphenol N	DPh	0.30	280–310	350	380
	DPhE	0.48	270–310	350	390
	DPhTE	0.45	290–300	360	390
	DPhM	0.76	275–290	340	380
Bromodiphenol C	DPh	0.23	280–305	310	340
	DPhE	1.00	280–295	300	330
	DPhTE	0.40	270–290	300	330
	DPhM	0.30	250–300	310	340
Bromodiphenol N	DPh	0.22	270–300	310	350
	DPhE	0.74	280–295	295	340
	DPhTE	0.42	260–290	295	320
	DPhM	0.25	255–295	300	320

^aT₁ = temperature of initial decomposition from the curve TGA (°C); T₂ = temperature maximum velocity of decomposition from the curve TGA (°C).

 TABLE VIII
 Temperature of Pressing: Mechanical and Electrical Properties of Polysulfonates

Test	DPhE	
	Diphenol C	Bromodiphenol C
Reduced viscosity (dL/g)	0.35	1.00
Temperature of pressing (°C)	210	215
Vicat softening point (°C)	151	188
Rupture strength (kg/cm ²)	—	110
Relative lengthening at rupture (%)	—	6
Dynstat impact strength (kg · cm/cm ²)	—	9.4
Bending strength (kg/cm ²)	—	173
Brinell hardness (kg/cm ²)	24.0	26.0
Dielectric constant	1.95	2.40
tan δ at 170 kHz (20°C)	0.0085	0.0615

at elevated temperature. The obtained results are shown in Table VIII.

CONCLUSIONS

Polysulfonates with reduced viscosity and high molecular weight were obtained by interfacial polycondensation. The most convenient conditions were found to be following: methylene chloride—an organic phase, stoichiometric quantities of reagents, temperature 25–27°C, aqueous to organic phase ratio 1 : 1.

The obtained polysulfonates show very high melting points and very good thermal and chemical stability. They are soluble in halogenated aliphatic hydrocarbons.

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