S0032-3861(96)00554-X

Synthesis of and physico-chemical studies on poly(4,4'-cyclopentylidene diphenylene toluene-2,4-disulfonate)

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(Received 17 November 1995; revised 3 May 1996)

Poly(4,4'-cyclopentylidene diphenylene toluene-2,4-disulfonate) (PSBPT) has been synthesized by conventional interfacial polycondensation of 1,1'-bis(4-hydroxyphenyl) cyclopentane (0.005 mol) and toluene-2,4-disulfonyl chloride (0.005 mol) using water (50 ml)–chloroform (12.5 ml) as interphase, alkali (0.015 mol) as acid acceptor and cetyltrimethyl ammonium bromide (0.125 g) as emulsifier. The structure of PSBPT has been supported by infra-red and nuclear magnetic resonance spectral data. A $40\,\mu m$ thick film has $200.1\,kg\,cm^{-2}$ tensile strength and 0.6% elongation at break. A 0.19 mm thick film has static hardness 14.5–$16.5\,kg\,mm^{-2}$ at different loads (15–60 g). The density ($1.353 \pm 0.0009\,g\,cm^{-3}$) of PSBPT has been determined by the floatation method and compared with calculated values ($1.3973\,g\,cm^{-3}$). Thermogravimetric (t.g.a.) and differential thermal (d.t.a.) measurements have been made at four different heating rates and $10°C\,min^{-1}$, respectively in N_2 atmosphere. D.t.a. showed the glass transition temperature T_g at about 134°C and two exotherms at 337°C and 362°C which might be due to decomposition. PSBPT is stable up to about 355°C in N_2 atmosphere and involves two-step degradation. The average energy of activation, pyrolysis order and frequency factor for step-I are $52.6\,kcal\,mol^{-1}$, 2.5 and $9.22 \times 10^{13}\,min^{-1}$, respectively. PSBPT has excellent hydrolytic stability towards acids and alkalis. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: cardo polymers; polycondensation; i.r.; n.m.r.; d.t.a.; t.g.a.; hydrolytic stability)

INTRODUCTION

The resistance to high temperature is increased considerably by introducing cardo (Latin meaning loop) groups in the main chain backbone[1]. The aromatic cardo polymers possess excellent thermal and chemical stability, excellent mechanical and dieletric properties, excellent solubility, high softening temperature and easy processability[2]. The polymers of varying stiffness[3] can be synthesized by using different kinds of disulfonyl chlorides and diphenols. Aromatic polysulfonates[3–14] are useful as thermoplastic moulding composition alone or mixed with fillers and can be made into films and fibres or used as coatings, adhesives and packaging. They possess unique stability towards hydrolytic attack[3–5,12]. The literature survey on aromatic polysulfonates revealed that not much work has been carried out on polysulfonates containing cardo groups. Thus, the literature survey on polysulfonates prompted us to investigate physicochemical properties of poly(4,4'-cyclopentylidene diphenylene toluene-2,4-disulfonate) (I) (see *Scheme 1*).

EXPERIMENTAL

Materials

The chemicals used were of laboratory grade and were purified prior to use[15]. Toluene-2,4-disulfonyl chloride (TDSC) was synthesized according to the literature
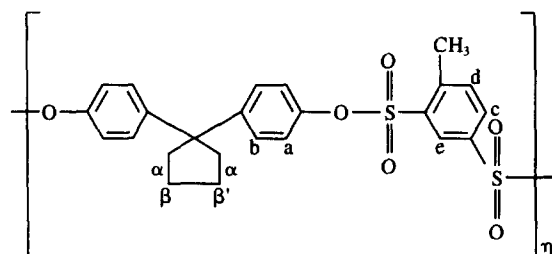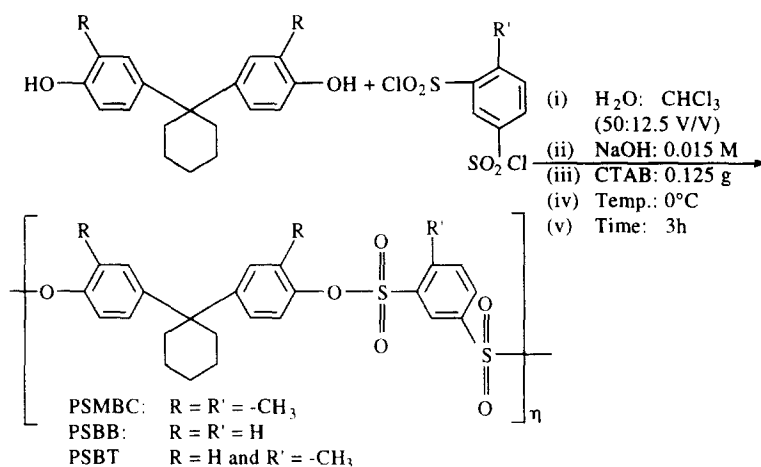

Scheme 1

method[16], 1,1'-bis(4-hydroxyphenyl)cyclopentane (BP) was synthesized from cyclopentanone and phenol using HBF_4 as catalyst and was repeatedly recrystallized from benzene till m.p. 154°C was obtained. The emulsifier cetyltrimethyl ammonium bromide (SISCO-chem) was used as such.

Polymer synthesis

Cardopolysulfonate-poly(4,4'-cyclopentylidene diphenylene toluene-2,4-disulfonate) (PSBPT) was synthesized by conventional interfacial polycondensation of BP and TDSC according to our previous publications[17,18] shown in *Scheme 2*.

The above mentioned cardopolysulfonates[17–20] are highly soluble in common organic solvents like chloroform, 1,2-dichloroethane, chlorobenzene, 1,4-dioxane, THF, etc. and form tough and transparent films from solutions. They possess excellent resistance to acids and alkalis, good thermal and mechanical properties and also possess moderate antibacterial activity.

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PSMBC: R = R' = -CH₃
PSBB: R = R' = H
PSBT: R = H and R' = -CH₃

Scheme 2

Aromatic polysulfonates[3] of the type $(-O_2S-Ar-SO_2-O-Ar-O-)_n$, where Ar is m-C_6H_4, $(p$-$C_6H_4)_2$, $(p$-$C_6H_4)_2O$, $(p$-$C_6H_4)_2CH_2$ and $(p$-$C_6H_4)_2SO_2$, have low degrees of crystallinity and limiting solubility in common organic solvents.

Film preparation

The thin and thick films of PSBPT were prepared according to our previous publication[17].

Characterization of PSBPT

The infra-red (i.r.) spectrum (thin film) of PSBPT was scanned on a Shimadzu DR-1, 435 i.r. spectrophotometer. The nuclear magnetic resonance (n.m.r.) spectrum of PSBPT was scanned in CDCl₃ on Hitachi R-1200 (60 MHz) spectrometer using TMS as internal standard. The mechanical testing and static hardness measurements were made on Instron, Model 1026 and a Universal Research Microscope, CZ NU2, respectively. The thermogravimetric analysis (t.g.a.) measurements at four different heating rates, namely 10, 20, 30 and $40°C\,min^{-1}$ and differential thermal analysis (d.t.a.) measurement at the heating rate of $10°C\,min^{-1}$ in N_2 atmosphere were made on a Perkin Elmer TGA and DTA, respectively. The densities of solutions were measured by the usual method.

RESULTS AND DISCUSSION

Spectral characterization

Figure 1 shows the i.r. spectrum (thin film) of PSBPT. The observed characteristic absorption bands[3,17,18,21] (cm⁻¹) are: 1383 ($-O-\overset{O}{\underset{O}{S}}-$,ν_s), 1371 (C–H δ_s, CH₃), 1179 ($-O-\overset{O}{\underset{O}{S}}-$, ν_{as}) and 1146 (C–H *i-p-d*, ArH) besides normal modes of the alkane, alicyclic and aromatic groups. *Figure 2* shows the n.m.r. spectrum (CDCl₃) of PSBPT. It is evident from *Figure 2* that there are five distinct signals[17,18]: three singlets at δ 1.385 (4H, β-CH₂-), δ1.888 (4H, α-CH₂-) and at δ2.51 (3H, -CH₃) and two multiplets at δ 7.287–6.418 (8H, *a* and *b* Ar–H) and at δ 7.888–7.433 (3H, *c*, *d* and *e* Ar–H). The residual solvent signal is overlapped at δ 7.295. Each type of proton is assigned in the spectrum itself. Thus, the structure of PSBPT is supported by i.r. and n.m.r. spectral data.

Mechanical properties

A 40 μm thick film of PSBPT has average tensile strength and % elongation at break are found to be $200.1\,kg\,cm^{-2}$ and 0.6, respectively. Comparative mechanical properties of PSBPT, with PSMBC, PSBB and PSBT, are reported in *Table 1*. From *Table 1* it is clear that the tensile strength of PSBPT is somewhat greater than that of PSMBC, but much smaller than PSBB and PSBT; and PSMBC is comparatively more elastic than the other three polysulfonates. Thermal and mechanical properties of polymers are dependent on the backbone structure as well as molecular weights.
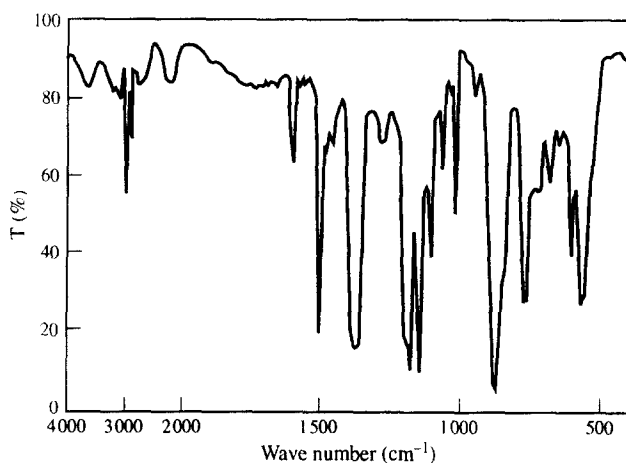

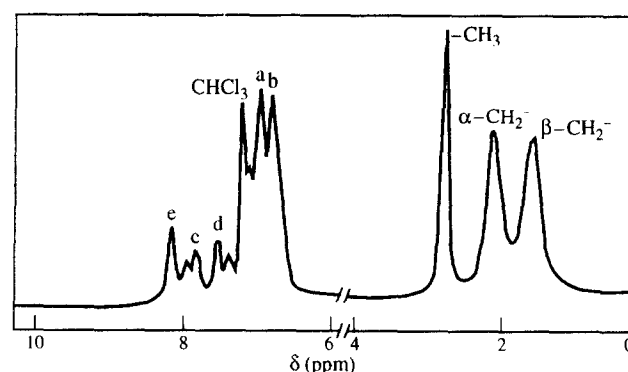**Figure 1** I.r. spectrum (thin film) of PSBPT

Figure 2 N.m.r. spectrum (CDCl₃) of PSBPT (60 MHz)

Table 1 A comparative mechanical properties of PSBPT with PSMBC[19], PSBB[18] and PSBT[18]

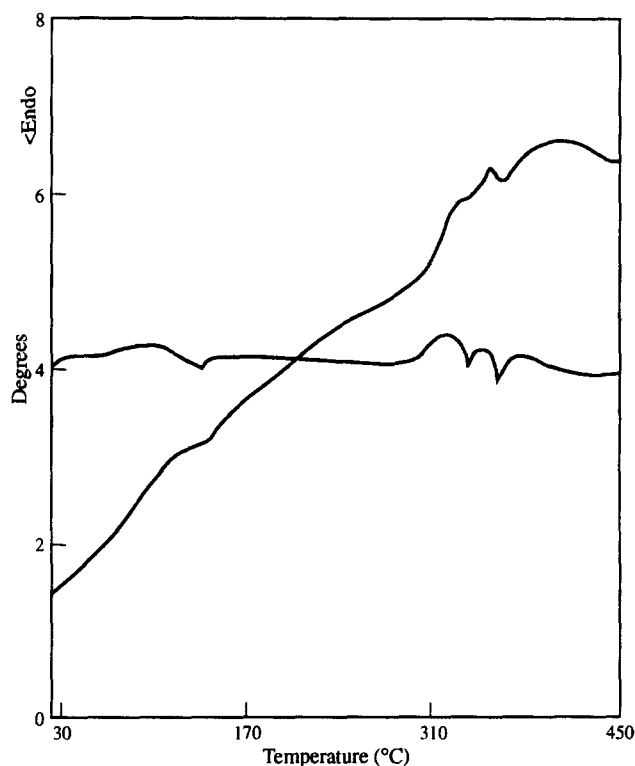| Property	PSBPT	PSMBC	PSBB	PSBT
Tensile strength $(kg cm^{-2})$ (thickness, μm)	200.1 (40)	170 (71)	1971 (40)	1677 (50)
% Elongation	0.6	5.2	1.3	1.2
Static hardness[a]	14.5–16.5	12.8–16.4	12.8–15.6	14.5–16.5
$(kg cm^{-2})$ (thickness, mm)	(0.190)	(0.192)	(0.178)	(0.190)

[a] At different loads (15–60 g)

Figure 3 D.t.a. thermogram of PSBPT at heating rate of $10°C min^{-1}$ in N_2

Aromatic carboxylate–sulfonate copolymers[9,11,14,22] containing rigid moieties such as biphenyl, biphenylsulfone, etc. have about three times better mechanical properties $(527–690 kg cm^{-2})$ than PSBPT and this may be due to the less rigid structure and low molecular weight of PSBPT.

The static hardness of PSBPT film of thickness 0.19 mm was determined at three different loads at room temperature ($\sim 33°C$). The indentation time was

20 s. The observed hardness $(kg mm^{-2})$ is found to be 16.5, 14.6 and 14.5, respectively at 15, 30, and 60 g loads and are also reported in *Table 1* which is comparable with other polymers containing cyclohexyl as cardo group.

Thermal properties

Different polymers decompose over different ranges of temperature yielding different proportion of volatile and residues. The decomposition reactions are time and temperature dependent[23]. *Figure 3* shows a d.t.a. thermogram of PSBPT at a heating rate of $10°C min^{-1}$ in N_2 atmosphere. The glass transition temperature (T_g) is observed at about 134°C, and is reported in *Table 2* along with that of the other polymers. The two exotherms observed at 337°C and 362°C which might be due to decomposition of PSBPT. From *Table 2* it is clear that the T_g of PSBPT is higher than that of other polysulfonates without cardo groups, except polysulfonates containing rigid moieties as cited in ref. 3.

The introduction of cardo groups in the polymer backbone endows very specific properties such as enhanced thermal stability, together with excellent solubility. T.g.a. is a useful analytical technique for understanding the chemical nature of the polymer. *Figure 4* shows t.g.a. thermograms of PSBPT at four different heating rates, namely 10, 20, 30 and $40°C min^{-1}$ in N_2 atmosphere. From *Figure 4* it is clear that thermograms are shifted towards higher temperature with increasing heating rate (β). The shape of the t.g.a. curve depends on the nature of the apparatus and the way in which it is used. It is also dependent on the kinetic parameters which are useful in understanding the degradation mechanism and the thermal stability of polymers[25–27]. From *Figure 4* it is clear that PSBPT is thermally stable up to about 355°C and involves two-step decomposition. The first step shows about 55% weight loss over the temperature range 360–400°C, and the

Table 2 A comparative glass transition temperature and thermal stability of polysulfonates with and without cardo groups

Bisphenol	Disulfonyl chloride	T_g (°C)	Thermal stability (°C)	Temp. of maximum degradation	Ref.
Bisphenol-A	4,4'-Disulfonylchloride diphenylether	110	–	–	24
HO–Ar–OH	ClO_2SArSO_2Cl	200–250	>200	–	3[a]
Bisphenol-A	m-Benzenedisulfonyl chloride	110–136	–	340–400	8
Bisphenol-B	m-Benzenedisulfonyl chloride	126–47	–	330–355	8
Bisphenol-C	m-Benzenedisulfonyl chloride	125–127	355	355–390 525–650	20
Bisphenol-C	Toluene-2,4-disulfonyl chloride	138–142	360	360–390 550–700	20
Methylsubstituted Bisphenol-C	Toluene-2,4-disulfonyl chloride	140	340	340–416 520–700	19
Bisphenol-P (1,1'-Bis(4-hydroxy phenyl)cyclopentane	Toluene-2,4-disulfonyl chloride	134	355	360–400 542–620	

[a] $Ar = m\text{-}C_6H_6, (p\text{-}C_6H_4)_2, (p\text{-}C_6H_4)_2O, (p\text{-}C_6H_4)_2CH_2, (p\text{-}C_6H_4)_2SO_2$
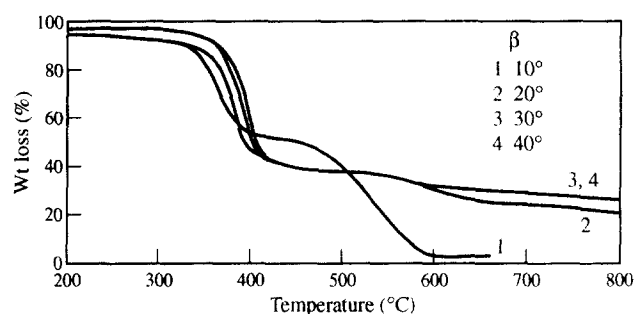
Figure 4 T.g.a. thermograms of PSBPT at different heating rates in N₂

second step shows about 72% weight loss over the temperature range 542–620°C. Moreover there is not much change in weight loss with heating rate above 20°C min^{-1} in the case of the second step. Ehlers *et al.*[25] have reported the thermal degradation of polyarylene sulfonate, poly(*p*-phenylenesulfide) and poly(arylenesulfone) in vacuum at 250–620°C and concluded that the most characteristic decomposition reaction is the almost complete removal of S as SO₂. The elimination of SO₂ practically completes at 450°C and 350°C in the case of polysulfone and polysulfonate, respectively. In the present case the temperature of maximum degradation is observed at about 365–70°C which is slightly higher than that of polysulfonates without cardo group. Thus, the T_g and thermal stability (*Table 2*) of cardopolymers are superior than those of other polysulfonates, except polymers containing rigid moieties such as biphenyl, biphenyl sulfone, etc., but their solubility is excellent compared with other polysulfonates.

The energy of activation for several degrees of fractional change (*C*) was determined according to the methods of multiple heating rates of Anderson[29], Ozawa[30] and Friedman[31] and are reported in *Table 3*.

From *Table 3* it is evident that E_a is different for different degrees of fractional change indicating different degradation mechanism. The apparent order of the degradation process for the first step is found to be 2.5, which indicates a complex degradation process. The frequency factor (*A*) is found to be 9.22×10^{13} min^{-1}. The degradation of polymers is complex and involves a variety of reactions such as chain cleavage, rearrangement of chain segments, decomposition of chain segments, cross linking, etc.

The sulfonate linkage is the weak point in the main chain which is responsible for the elimination of SO₂. Following decomposition of the sulfonate linkage, hydrogen abstraction would occur which would result in a crosslinked residue consisting of aromatic rings. This would be expected to degrade at elevated temperatures. The degradation product may be benzene, toluene, cyclopentane and many other hydrocarbons.

Density measurements

The density, ρ, of **PSBPT** was determined by the flotation method using a CCl₄–n-hexane system at 30°C. The composition of the two solvents was adjusted in such a way that the film just remained suspended throughout. The density of the mixture was determined after 24 h by the usual method. The average of six measurements was found to be 1.3530 ± 0.0009 g cm^{-3}.

The density of **PSBPT** was also calculated employing the structural aspects[32]

$$\rho = \frac{KM}{N_A \sum_i \Delta V_i}$$

Where K (0.695) is the packing coefficient, M (470) is the repeat unit molecular weight, N_A is Avogadro's number and $\Sigma_i \Delta V_i$ (388.14 Å^3) is the intrinsic volume of the repeat unit. The calculated density is found to be

Table 3 The energy of activation E_a, apparent order of the reaction and frequency factor A for PSBPT

Degree of fractional change,	E_a (kcal mol^{-1})				
C	Anderson[27]	Ozawa[28]	Friedman[29]	*n*	*A*
0.1	31.8	29.4	28.9		
0.2	42.5	40.3	40.2		
0.3	49.4	46.8	47.2	2.5	9.22×10^{13}
0.4	59.3	55.8	56.0		
0.5	59.3	55.9	56.3		

Table 4 Hydrolytic stability of PSBPT towards acids and alkalis at room temperature

	% Wt loss						
10%	After 7 days			After 1 month			After refluxing for 24 h
Acid/alkali	PSBPT	PSBB	PSBT	PSBPT	PSBB	PSBT	PSMBC
H₂SO₄	0.60	1.00	0.65	1.20	1.60	0.94	100.00
HCl	0.70	0.75	1.00	1.50	0.83	1.44	
HNO₃	1.40	0.75	0.90	1.40	0.97	1.18	14.1
CH₃COOH	1.40			1.40			
NaOH	2.10	0.35	0.25	2.10	0.58	0.40	0.70
KOH	2.50	0.50	0.34	2.50	0.56	0.36	

$1.3973\,\mathrm{g\,cm^{-3}}$. The comparison of experimental and calculated density values indicates the right choice of packing coefficient with a relative error of -3.1%.

Acid and alkali resistance

Aromatic polysulfonates are thermoplastic materials having unique stability towards hydrolytic attack[3,5,12]. The hydrolytic stability of PSBPT films was determined at room temperature in 10% each of aqueous sulfuric acid, nitric acid, hydrochloric acid, acetic acid, sodium hydroxide and potassium hydroxide. The % weight loss after 7 days and after 1 month were determined and are reported in *Table 4* along with PSMBC[19], PSBB[20] and PSBT[20]. The polysulfonates[3] of the type $(-O_2S-Ar-SO_2-O-Ar-O-)_n$ (where Ar is m-C_6H_4, $(p$-$C_6H_4)_2$, p-$(C_6H_4)_2O$, $(p$-$C_6H_4)_2CH_2$ and $(p$-$C_6H_4)_2SO_2)$ possess hydrolytic stability towards acids and bases at room temperature. The hydrolytic stability of carboxylate-sulfonate copolymers[9] showed % changes in weight: -6.0, 3.0, and 6.0 after refluxing for 20 h in 10% Na_2CO_3, 1 week in 10% NH_3 and 1 week refluxing in 15% HCl, respectively. The acid and alkali resistance of PSBPT is excellent and comparable with other cardopolysulfonates and polysulfonates containing rigid moieties[3,9].

In conclusion PSBPT possesses excellent solubility in common solvents, good thermal and mechanical properties and excellent hydrolytic stability towards acids and alkalis.

REFERENCES

1 Korshak, V. V., Vinogradova, S. V. and Vygodskii, Ya. *J. Macromol. Sci., Rev. Macromol. Chem.* 1974, **11**, 45
2 Johnson, R. N., Farnham, A. G., Glendining, R. A., Hale, W. E. and Merriam, C. N. *J. Polym. Sci., Part A-1* 1967, **5**, 2375
3 Thomson, D. W. and Ehlers, G. F. L. *J. Polym. Sci.* 1964, A2 **3**, 1051
4 Goldberg, E. P. and Scardiglia, F., U.S. 1966, 3, 271, 368; *Chem. Abstr.* 1967, **66**, 3015
5 Vizgert, R. V., Budenkova, N. M. and Maksimenko, N. N. *Vysokomol. Soedin Ser. A*, 1989, **31**, 1379; *Chem. Abstr.* 1990, **112**, 21 352
6 Borg Warner Corporation, Brit. 1965, 1 015 202; *Chem. Abstr.* 1966, **64**, 8417
7 Goldberg, E. P. and Scardiglia, F., U.S. 1966, 3 262, 914; *Chem. Abstr.* 1966, **65**, 15 539
8 Fontan, Y. J., Laguna, O. and Shih, J. *J. An. Quim. 1968*, **64**, 389; *Chem. Abstr.* 1968, **69**, 19 647
9 Borg Warner Corporation, Fr. 1968, 1 521 342; *Chem. Abstr.* 1969, **70**, 115 696
10 Hata, N. and Takase, Y. Jp. 1974, 7 432 797; *Chem. Abstr.* 1975, **82**, 125 845
11 Schlott, R. J., Scardiglia, F., Goldberg, E. P. and Hoeg, D. F. *Macromol. Synth.* 1972, **4**, 59
12 Schlott, R. J., Goldberg, E. P., Scardiglia, F. and Hoeg, D. F. *Adv. Chem. Ser.* 1969, **91**, 703
13 General Electric Company, Neth. Appl. 1966, **6**, 600 874; *Chem. Abstr.* 1967, **66**, 19 035
14 Goldberg, E. P. and Scardiglia, F., Brit. 1969, 1 151 599; *Chem. Abstr.* 1969, **71**, 30 834
15 Weisberger, A. and Proskaur, E. S. (Eds) 'Techniques of Organic Solvents', Interscience, New York, 1955
16 Spryskov, A. A. and Yakovleva, T. I. *Zhur. Obschchei Khim.* 1955, **25**, 783; *J. Gen. Chem. USSR*, 1955, **25**, 749; *Chem. Abstr.* 1956, **50**, 2463
17 Kamani, M. M. and Parsania, P. H. *J. Polym. Mater.* 1995, **12**, 217
18 Desai, J. A., Dayal, U. and Parsania, P. H. *J. Macromol. Sci.-Pure Appl. Chem.* 1996, **A33**, 1113
19 Kamani, M. M. and Parsania, P. H. *J. Polym. Mater.* 1955, **12**, 223
20 Desai, J. A. and Parsania, P. H. (Communicated)
21 Parikh, V. M. 'Absorption Spectroscopy of Organic Molecules' Addison-Wesley, London, 1978
22 Borg Warner Corporation, Fr. 1965, 1 419 852; *Chem. Abstr.* 1966, **65**, 10 743
23 Kolthoff, I. M. 'Treatise on Analytical Chemistry', Part 3, Interscience, New York, 1976, p. 393
24 Conix, A. and Laridon, U. L. Belg. 1958, 56 547; *Chem. Abstr.* 1961, **55**, 25 356
25 Levi, D. W., Reich, L. and Lee, H. T. *Polym. Eng. Sci.* 1965, **5**, 135
26 Friedman, H. L. *Chem. Abstr.* 1961, **55**, 26 511
27 Reich, L. and Levi, D. W. *Makromol. Chem.* 1963, **66**, 102
28 Ehlers, G. F. L., Fisch, K. K. and Powell, W. R. *J. Polym. Sci., Part A-1* 1969, **7**, 2955
29 Anderson, H. C. *J. Polym. Sci.* 1964, **C6**, 175
30 Ozawa, T. *Bull. Chem. Soc. Jap.* 1965, **38**, 1881
31 Friedman, H. L. *J. Polym. Sci.* 1964, **C6**, 183
32 Slonimskii, G. L., Askadskii, A. A. and Kitagorodskii, A. I. *Polym. Sci. USSR* 1970, **A12**, 556