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RESEARCH ARTICLE

Synthesis of and thermal properties studies on Poly (4, 4' – Cyclopentylidene diphenylene toluene – 2, 4 - disulfonate

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ABSTRACT

Poly (4, 4'-Cyclopentylidene diphenylene toluene – 2,4-disulfonate) (PSBPCT) has been Synthesized by Conventional interfacial poly condensation of 1, 1'-bis (4-hydroxyphenyl) cyclopentane (0.005 mol) and toluene-2, 4-disulfonyl chloride (0.005 mol) using water (50 ml) – chloroform (10ml) as inter phase, alkali (0.015 mol) as acid acceptor and cetyltrimethyl ammonium bromide (0.125g) as emulsifier. The structure of compounds has been supported by Infra-red and nuclear magnetic resonance spectral data. Thermogravimetric (t.g.a.) measurement has been made at four different heating rates and 10^0C min^{-1}, respectively in N_2 atmosphere. PSBPCT is stable up to about 355^0C in N_2 atmosphere and involves two-step degradation.

KEYWORDS

Cardo polymers, polycondensation, Infrared Radiation, Nuclear Magnetic Resonance, Thermal Gravimetric Analysis

INTRODUCTION

The resistance to high temperature is increased considerably by introducing cardo (Latin meaning loop) groups in the main chain back bone.[1] The aromatic Cardo Polymers Possess excellent thermal and chemical stability. The polymers of varying stiffness.[3] can be synthesized by using different kinds of disulfonyl chlorides and diphenols. Aromatic Polysulfonates[3-14] are useful at thermo plastic moulding composition alone or mixed with fillers and can be made into films and fibres or used as coatings, adhesives and packaging. They possess uniques stability towards bydrolytic attack.

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The literature survey on aromatic polysulfonates revealed that not much work has been carried out on polysulfonates containing cardo groups.

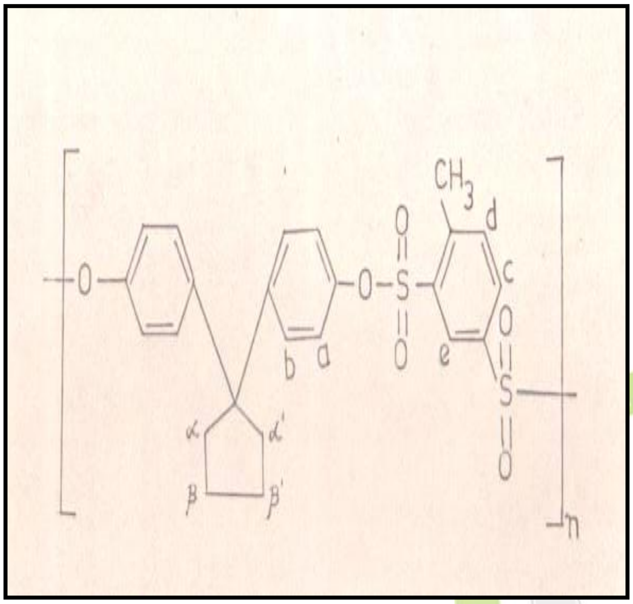
Thus, the literature survey on polysulfonates prompted us to investigate physico chemical properties of Poly (4,4'-Cyclopentylidene diphenylene tolune-2, 4-disulfonate) (I) (See Scheme-I)

EXPERIMENTAL

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 method.[16] 1,1-bis(4-hydroxyphenyl) Cyclopentane (BP) was synthesized from cyclopentanone and phenol using HBF4 as catalyst and was repeatedly recrystallized from benzone till m.p. 154^0C was obtained. The emulsifier cetyltrimethyl ammonium bromide (SISCO-Chem) was used as such.

Polymer Synthesis

Cardo Polysulfonate-Poly (4,4'-Cyclopentylidiene diphenylene toluene-2, 4-disulfonate) (PSBPCT) was synthesized by conventional interfacial poly condensation of BP and TDSC.



The above mentioned cardo polysulfonates 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.

Characterization of PSBPCT

The infra-red (IR) spectrum (thin film) of PSBPCT was acanned ona shimadzu DR-1, 435 ir, spectrophoto meter. The nuclear magnetic resonance (n.m.r.) spectrum of PSBPCT was scanned in $CDCl_3$ on Hitachi R-1200 (60 MH2) spectometer using TMS as internal standard. The thermogravimetric analysis (t.g.a.) measurements at four different heating rates, namely 10, 20, 30 and 40^0C min^{-1} was made on a perkin Elmer TGA.

RESULTS AND DISCUSSION

Spectral Characterization

Figure-I show the i.r. spectrum (thin film) of PSBPCT. The observed characteristic absorption bands.[3,17,18,21]

(cm^{-1}) are : 1384 (-0- S-, γs), 1371 (C-H γs, -CH3) 1179(-0-S-, γas) and (C-H i-p-d, ArH) besides normal modes of the alkane, alicyclic and aromatic groups.

Figure: II Shows the n.m.r. Spectrum (CDCl3) of PSBPCT. It is evident from figure 2 that there are five distinct signals.17-18 three singlets at δ 1.385 (4H, β $-CH_2-$), δ 1.888 (4H, α-CH_2-) and at δ 2.51 (3H, - CH_3) and two multiplets at δ 7.287-6.418 (8H, 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 PSBPCT is supported by i.r. and n.m.r. Spectral data.

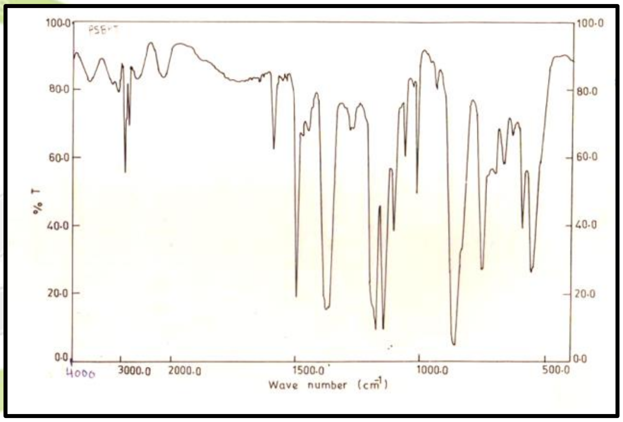


Figure 1: I.R. Spectrum (thin film) of PSBPCT

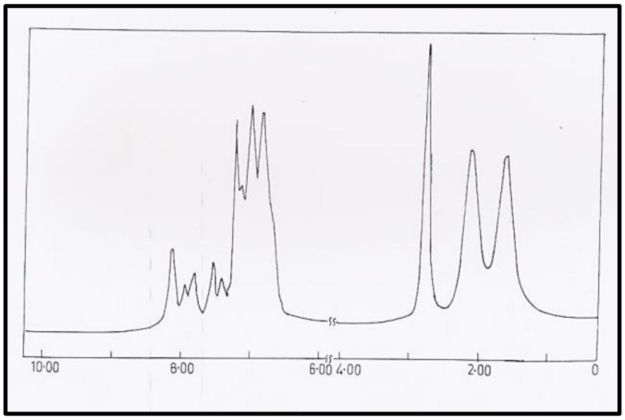


Figure 2: n.m.r. specturm ($CDCl_3$) of PSBPCT (60 MHz)

Thermal Properties

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 plymer. Figur-3 shows t.g.a thermograms of PSBPCT at four different heating rates, namely 10, 20, 30 and 40^{0}C min^{-1} in N_2 atmosphere.

From Figure-3 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.[11]

From Figure-3 it is clear that PSBPCT is thermally stable up to about 355^{0}C and involves two step decomposition. The first step shows about 55% weight loss over the temperature range 360-400^{0}C, and the second step shows 72% weight loss over the temperature range 542-620^{0}C.

Moreover there is not much change in weight loss with heating rate above 200C min^{-1} in the case of second step. Ehlers et al[11] have reported the thermal degradation of polyarylene sulfonate, poly (P-phenyl enesulfide) and Poly (arylenesulfone) in vacuum at 250-620^{0}C and concluded that the most characteristic decomposition reaction is the almost complete removal of S as SO_2. The elimination of SO_2 proctically complete at 450^{0}C and 350^{0}C in the case of polysulfone and polysulfonate, respectively.

In the present case the temperature of maximum degradation is observed at about 365-70^{0}C which is slightly higher than that of polysulfonates without cardo group.

Thus the thermal stability of cardo polymers are superior than those of other poly sulfonates, except polymers containing rigid moieties such as biphenyl, biphenyl sulfonate, etc., their solubility is excellent compared with other polysulfonate.

The energy of activation for several degrees of fractional change (C) was determined according to the methods of multiple heating rates of Anderson. Ozawa and Friedman and are reported in table-1.

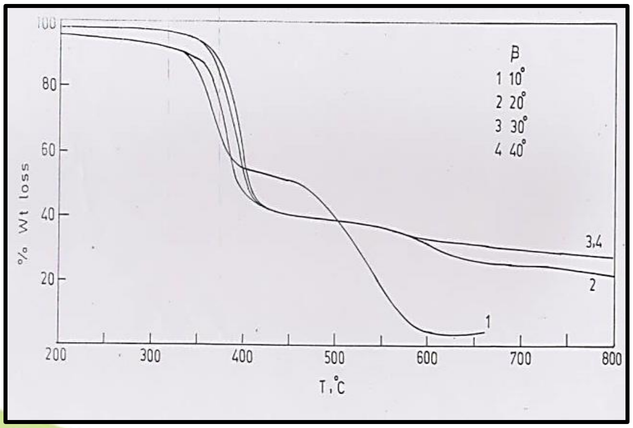


Figure 3: T.g.a. thermograms of PSBPCT at different heating rate in N_2

From Table-1 it is evident that Ea is different for different degree of factional 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 x 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 SO_2, following decomposition of the sulfonate linkage, hydrogen abstraction would occur which would result in a cross linked 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.

In conclusion PSBPCT possesses excellent solubility in common solvents, good thermal properties.

Table 1: The energy of activation Ea, apparent order of the reaction and Frequency Factor A for PSBPCT

Degree of Fractional Charge C	**Ea (K cal mol^{-1})**				
	Anderson	**Ozawa**	**Friedman**	**n**	**A**
0.1	31.8	29.4	28.9	2.5	9.22x1023
0.2	42.5	40.3	40.2		
0.3	49.4	46.8	47.2		
0.4	59.3	55.8	56.0		
0.5	59.3	55.9	56.3		

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