Journal of Macromolecular Science, Part A

Electrical, Mechanical, and Thermal Properties of Poly(4,4'-Cyclohexylidene Diphenylene-*m*-Benzene/Toluene-2,4-Disulfonate)

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ELECTRICAL, MECHANICAL, AND THERMAL PROPERTIES OF POLY(4,4′-CYCLOHEXYLIDENE DIPHENYLENE-*m*-BENZENE/TOLUENE-2,4-DISULFONATE)

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ABSTRACT

The films of poly(4,4′-cyclohexylidene diphenylene-*m*-benzene disulfonate) (PSBB, 0.610 mm thick) and poly(4,4′-cyclohexylidene diphenylene–toluene-2,4-disulfonate) (PSBT, 0.537 mm thick) showed 8.23 ± 0.25 and 9.6 ± 0.245 kV, respectively, as the dielectric breakdown voltage (ac) in air at room temperature. The same films have 8.8 × 10^{11} and 7.2 × 10^{14} $\Omega \cdot$cm volume resistivity. PSBB (40 μm thick) and PSBT (50 μm thick) films have tensile strengths of 1971 and 1677 kg/cm^2 and percent elongations of 1.3 and 1.2, respectively. The static hard

nesses of PSBB (0.178 mm thick) and PSBT (0.190 mm thick) at three different loads (15–60 g) are 12.8–15.5 and 14.5–16.5 kg/mm^2, respectively. PSBB and PSBT are thermally stable up to about 355°C in an N$_2$ atmosphere and involve two-step degradation. DSC and DTA showed T_g at about 125–127 and 138–142°C, respectively, for PSBB and PSBT in N$_2$. PSBB and PSBT have comparable breakdown voltages and volume resistivity with some useful plastics whereas they have superior T_g and thermal stability with retention of excellent solubility in common solvents over polysulfonates without a cardo group. Thus, the cardo (cyclohexyl) group has enhanced thermal and mechanical properties with excellent solubility and easy processing.

INTRODUCTION

Aromatic polysulfonates are analogs of polyarylates. Polymers of varying stiffness [1] can be synthesized from the more rigid aromatic moieties like biphenyl and biphenyl sulfone. The softening temperature (100–160°C) of the polysulfonates of unsubstituted bisphenols respond to structural changes in the arylene units in much the same way as those of polyarylates. Substitution ortho to the phenol function markedly raises the softening temperature. Polysulfonates soften over a considerably broad temperature range and always lower than those of the corresponding carboxylate polyarylates [2]. The resistance to high temperature can be increased considerably by introducing cardo (Latin meaning, loop) groups in the main chain backbone [3]. Aromatic polysulfonates are well known for their unique stability toward hydrolytic attack [1, 4–7] and are useful for coatings, adhesives, and packaging [8–11]. A literature survey on aromatic polysulfonates revealed that not much work has been carried out on polysulfonates containing cardo groups. This prompted us to study the thermal, mechanical, and electrical properties of poly(4,4′-cyclohexylidene diphenylene-*m*-benzene disulfonate) (PSBB) and poly-(4,4′-cyclohexylidene diphenylene–toluene-2,4-disulfonate) (PSBT).

PSBB : R =   R' = H

PSBT : R = CH$_3$, R' = H

PSMBC : R = R' = CH$_3$
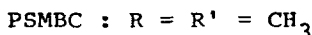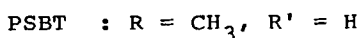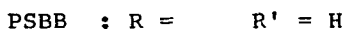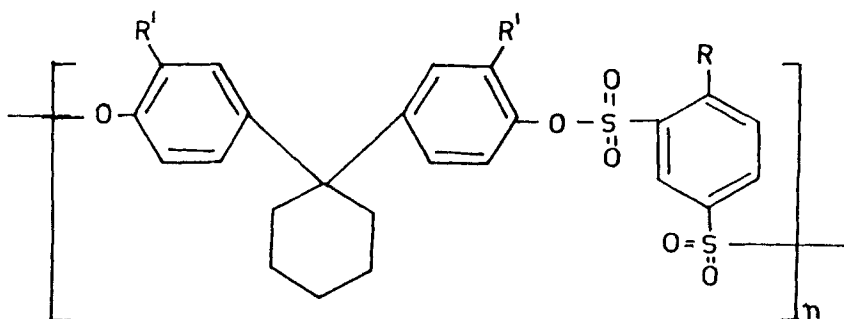
EXPERIMENTAL

Materials

Cardo Polysulfonates

Poly(4,4'-cyclohexylidene diphenylene–*m*-benzene disulfonate) (PSBB) and poly(4,4'-cyclohexylidene diphenylene–toluene-2,4-disulfonate) (PSBT) used in the present study were synthesized and purified according to our previous work [12]. Tough and transparent films of PSBB and PSBT were cast from ~5% chloroform solutions and dried according to our previous publication [13].

Measurements

Mechanical testing and static hardness testing were made on an Instron Model-1026, and on a Universal Research Microscope, CZ, NU2, respectively.

The dielectric breakdown voltage (ac) measurements were made on a Voltage Breakdown Tester (Allied Electrical Industries, Baroda) at room temperature in air using 6-mm diameter brass electrodes according to the ASTM D 149-92 method. The volume resistivity measurements were made on a volume resistance conductivity bridge according to the ASTM D 257-92 method. The differential scanning calorimetric (DSC) and differential thermal analysis (DTA) at the heating rate of 10°C/min, and thermogravimetric (TG) measurements at four different heating rates (10, 20, 30, and 40°C/min) were made, respectively, on Mettler DSC, DTA, and Perkin-Elmer.

RESULTS AND DISCUSSION

Electrical and Mechanical Properties

0.61-mm PSBB and 0.537-mm PSBT thick films have 8.23 ± 0.25 kV (343 V/mil) and 9.60 ± 0.245 kV (454 V/mil) breakdown voltages, respectively, in air at room temperature and are reported in Table 1 in terms of dielectric strength along with some useful industrial plastics [14]. The breakdown voltage is influenced by the duration and rate of voltage application, thickness of the sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes, and the nature of the prevailing environment. The properties of cardo polymers [3] depend on the backbone structure. The presence of cardo groups in different hetero- and carbo-chain polymers endow them with very specific properties: enhanced thermal stability together with excellent solubility, high flexibility, high thermal and chemical stability, good mechanical and dielectric properties. From Table 1 it is clear that PSBB and PSBT have dielectric strengths comparable with other useful plastics, which signifies the usefulness of these polymers.

Most high polymeric materials are very good to excellent insulating materials and they are less subject to conduction by imperfection and structural irregularities than other types of insulating materials such as ceramics. The volume resistivities of PSBB and PSBT films are also reported in Table 1 along with other plastics. Relative humidity affects the volume resistance of different insulators to a markedly different extent. Nonpolar polymers are unaffected by moisture, but polar organic

TABLE 1.   Comparative Dielectric Strength and Volume
Resistivity of Some Useful Plastics [14], PSBB, and PSBT

Plastic	Dielectric strength, V/mil	Volume resistivity, $\Omega \cdot cm$
Acrylics	450–550	$> 10^{14}$
Cellulose acetate	260–365	10^{10}–10^{13}
Cellulose acetate butyrate	250–400	10^{10}–10^{12}
Cellulose propionate	300–450	10^{12}–10^{15}
Nylon-6	440–510	10^{12}–10^{13}
Nylon-66	385–470	0.45–4×10^{14}
Unfilled phenolformaldehyde	300–400	10^{11}–10^{12}
Phenolformaldehyde (wood flour/cotton flock)	200–425	10^{9}–10^{12}
Polyacetal	465	6×10^{14}
Polycarbonates	400	2.1×10^{16}
PVC (rigid)	425	10^{13}
PSBB	343	8.8×10^{11}
PSBT	454	7.2×10^{14}

polymers are measurably affected by moisture. The extent to which polymers are affected by moisture is dependent on the degree of their moisture absorption and consequent solvation. Porosity favors moisture absorption and lowers the volume resistance. From Table 1 it is clear that PSBB and PSBT have comparable volume resistivities with other plastics except polyacrylics and polycarbonates. Thus, upon comparing the dielectric strengths and volume resistivities of PSBB and PSBT with other useful plastics, they signify their usefulness as dielectrics and insulating polymers.

The average tensile strength and % elongation of 0.178 mm PSBB and 0.190 mm PSBT thick films are reported in Table 2 along with poly(3,3'-dimethyl-4,4'-cyclohexylidene diphenylene–toluene-2,4-disulfonate), hereafter designated as PS-

TABLE 2.   Comparative Tensile Strength and Percent
Elongation of PSBB, PSBT, and PSMBC [13]

Polymer	Tensile strength, kg/cm^2 (Thickness, μm)	% Elongation
PSBB	1971 (40)	1.3
PSBT	1677 (50)	1.2
PSMBC	170 (71)	1.2

MBC [13]. From Table 2 it is clear that the tensile strengths of PSBB (1971 kg/cm^2) and PSBT (1677 kg/cm^2) are superior to that of PSMBC (170 kg/cm^2), whereas PSMBC is more elastic than PSBB and PSBT. This might be due to the low molecular weights of PSMBC chains although they are structurally almost the same since thermal and mechanical properties are dependent on the backbone structure and molecular weights. Comparing the tensile strengths of PSBB and PSBT with aromatic carboxylate–sulfonate copolymers [15–18] (527–690 kg/cm^2) containing rigid moieties such as biphenyl and biphenyl sulfone, it is observed that PSBB and PSBT have more than twice the tensile strengths. This surprising enhanced tensile strength might be due to incorporation of a cardo group (cyclohexyl) in the main backbone chain, as stated earlier.

The static hardnesses of 0.178 mm PSBB and 0.190 mm PSBT thick films were determined at three different loads at room temperature (33 °C) with an indentation time of 20 seconds. The observed hardness values are reported in Table 3 along with PSMBC [13]. From Table 3 it is clear that there is not much change in hardness with load and that the values are comparable with PSMBC. The hardness of the material depends on the shape and properties of the indentor.

The response of polymers to stress depends on their backbone structure, configuration, molecular weight, orientation, crystallinity, processing conditions, atmospheric conditions, etc. PSBB, PSBT, and PSMBC have almost the same abovementioned conditions and therefore they are expected to have almost identical hardness values.

Thermal Properties

Thermal studies of polymers can predict a polymer's performance in use and throw light on molecular architecture. Different polymers decompose over different ranges of temperatures, yielding different volatile and residue proportions. The decomposition reactions are time and temperature dependent [19]. In order to evaluate the glass transition temperatures, thermal stabilities, crystallizabilities, and kinetic parameters, PSBB and PSBT were analyzed by DSC, DTA, and TGA in an N$_2$ atmosphere. A typical DSC thermogram of PSBT at a heating rate of 10°C/min is shown in Fig. 1. DSC thermograms showed T_g at about 125 and 142°C, and exotherms at about 382 and 390°C, respectively, for PSBB and PSBT (Table 4). The

TABLE 3.   Static Hardness of PSBB, PSBT, and PSMBC [13] Films at Different Loads

	Hardness, kg/mm^2			Hardness, kg/mm^2, PSMBC[a] (0.192 mm)
Load, g	PSBB (0.178 mm)	PSBT (0.190 mm)	Load, g	
15	15.45	16.54	20	16.4
30	14.80	14.64	40	12.8
60	12.77	14.48	60	15.0

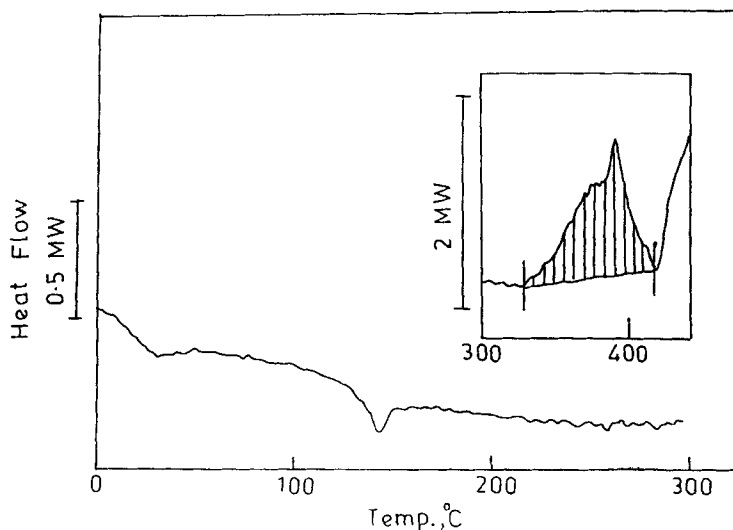[a]Time of indentation: 15 seconds at 32°C.

FIG. 1.   A typical DSC thermogram of PSBT at the heating rate of 10°C/min in N_2 atmosphere.

exotherms are due to partial crystallization followed by decomposition of PSBB and PSBT chains. DTA thermograms (Fig. 2) at a heating rate of 10°C/min showed T_g at about 125 and 138°C, respectively, for PSBB and PSBT. From Table 4 it is clear that T_gs of PSBB and PSBT are somewhat higher than those of other polysulfonates without cardo groups except polysulfonates containing rigid moieties like biphenyl and biphenyl sulfone [1] which possess low degrees of crystallinity and have limited solubilities in common solvents. PSBB and PSBT possess excellent solubilities [12] in common solvents and have excellent chemical resistances. It is also evident from Table 4 that substitution ortho to the sulfonate linkage markedly increases the T_g (PSBT and PSMBC).

TGA is a useful analytical technique for understanding the degradation behavior of polymers and has been proven useful for the evaluation of kinetic parameters of various reactions and materials which in turn provide valuable quantitative information about the stabilities of materials. Figures 3 and 4 show TG thermograms of PSBB and PSBT at four different heating rates: 10, 20, 30, and 40°C/min. From Figs. 3 and 4 it is evident that PSBB and PSBT are thermally stable up to about 355-60°C and have a two-step degradation. The thermograms shift to a higher temperature range with increasing heating rate (β). The thermal stability and temperature of maximum degradation ranges of PSBB and PSBT are reported in Table 4 along with polysulfonates without cardo groups. The shape of TG curves depends on the nature of the degradation reaction, activation energies (E_a), order of the reaction (n), etc., which are useful in understanding the degradation mechanism and thermal stability of polymers [20–22]. The characteristic TG curves of a given polymer are a function of polymer structure because of the unique sequence of physicochemical reactions which occur over definite temperature ranges.

In the present case the temperature of maximum degradation is observed at about 375 and 385°C, respectively, for PSBB and PSBT, which is slightly higher

TABLE 4. Comparative Glass Transition Temperature and Thermal Stability of Polysulfonates With and Without Cardo Groups

| Bisphenol	Disulfonyl chloride	T_g, °C	Thermal stability, °C	Temperature of maximum degradation	Ref.
Bisphenol-A	4,4′-Disulfonyl chloride diphenyl ether	110	–	–	27
HO-Ar-OH	Cl$_2$SO-Ar-SO$_2$Cl	200–250	>200	–	1
Bisphenol-A	m-Benzene disulfonyl	110–136	–	340–400	28
Bisphenol-B	m-Benzene disulfonyl chloride	126–147	–	330–355	28
Methyl substituted bisphenol-C	Toluene-2,4-disulfonyl chloride	138–140	340	340–416	13
				520–700	
Bisphenol-C	m-Benzene disulfonyl chloride	125–127	355	355–390	–
				550–650	
Bisphenol-C	Toluene-2,4-disulfonyl chloride	138–142	360	360–390	–
				550–700	
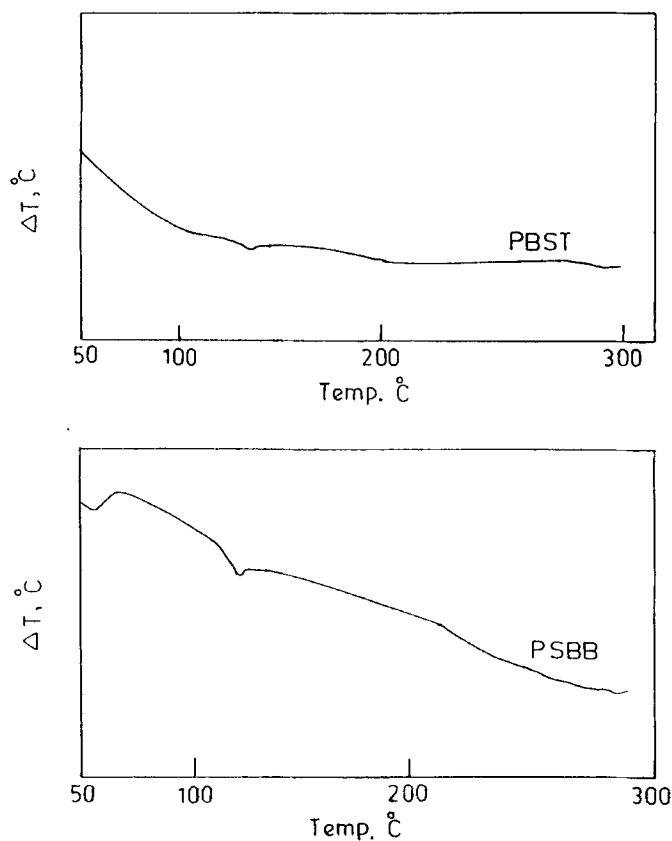
FIG. 2.   DTA thermograms of PSBB and PSBT at the heating rate of 10°C/min in N_2 atmosphere.

than that of polysulfonates without cardo group. From Table 4 it is clear that the T_gs and thermal stabilities of PSBB and PSBT are improved to some extent by introducing cyclohexyl as a cardo group with the retention of excellent solubility in common solvents.

Various methods have been proposed to estimate kinetic parameters. In the present investigation the energy of activation for several degrees of fractional change (C) was determined according to methods of multiple heating rates of Anderson [24], Ozawa [25], and Friedman [26]. They are reported in Table 5, from which it is evident that E_a is different for different degrees of fractional change, which indicates different degradation mechanisms. The apparent order of the degradation reaction (n) and frequency factor (A) for the first step are reported in the footnotes of Table 5. The values of n and A were not determined for the second step due to the complexity of the curves.

The degradation of polymers is complex and involves a variety of reactions such as chain cleavage, rearrangement of chain segments, decomposition of chain segments, crosslinking, etc. The sulfonate linkage is the weak point in the main
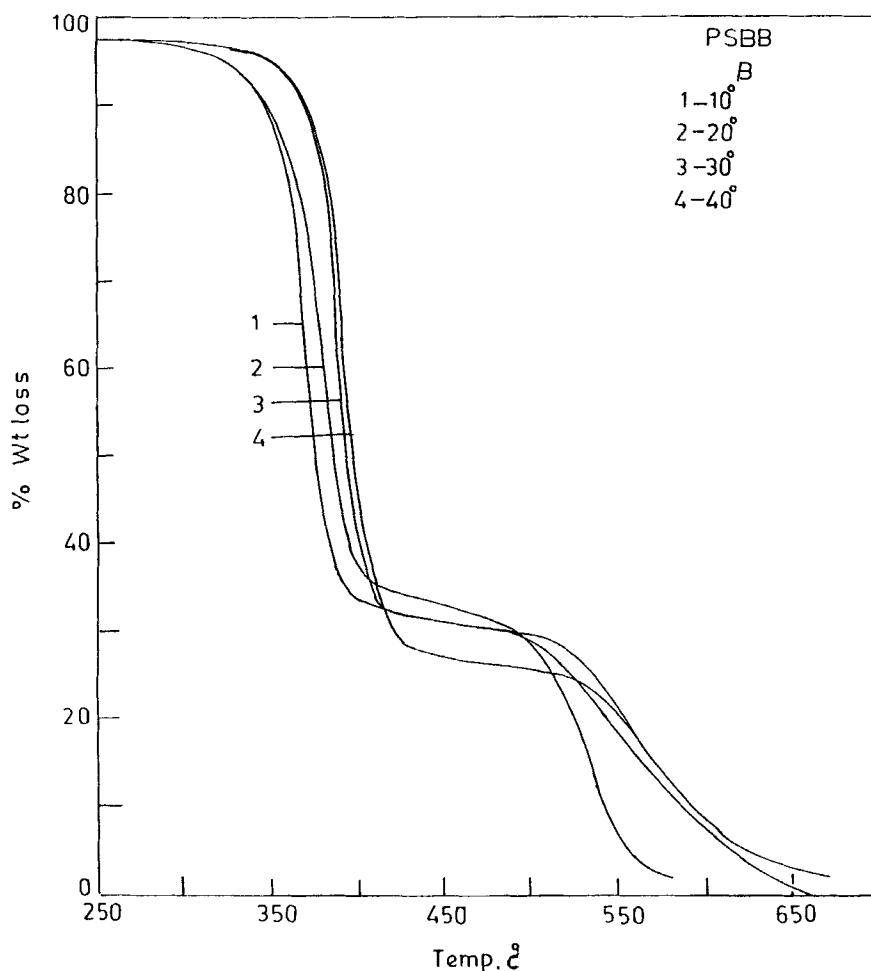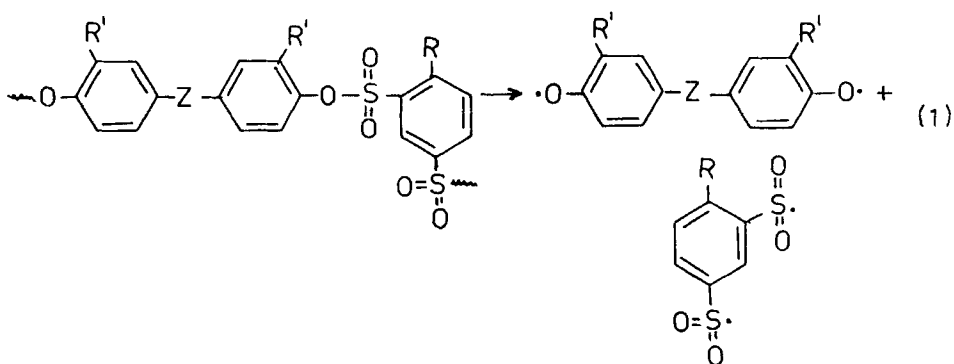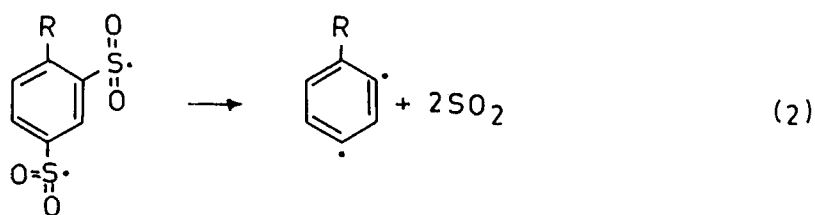
FIG. 3.   TG thermograms of PSBB at four different heating rates in N_2 atmosphere.

chain and therefore it degrades selectively, and S is eliminated as SO_2 [23]. The principal degradation reactions for the first step may be summarized as follows:

$$(1)$$

$$ \text{(diradical structure)} \longrightarrow \text{(diradical structure)} + 2SO_2 \qquad (2) $$

The diradicals formed above may be combined to give new products which further degrade at elevated temperature to give CO, CO_2, and hydrocarbons. It is presumed from the residual weight loss (Figs. 3 and 4) that no crosslinking occurred.
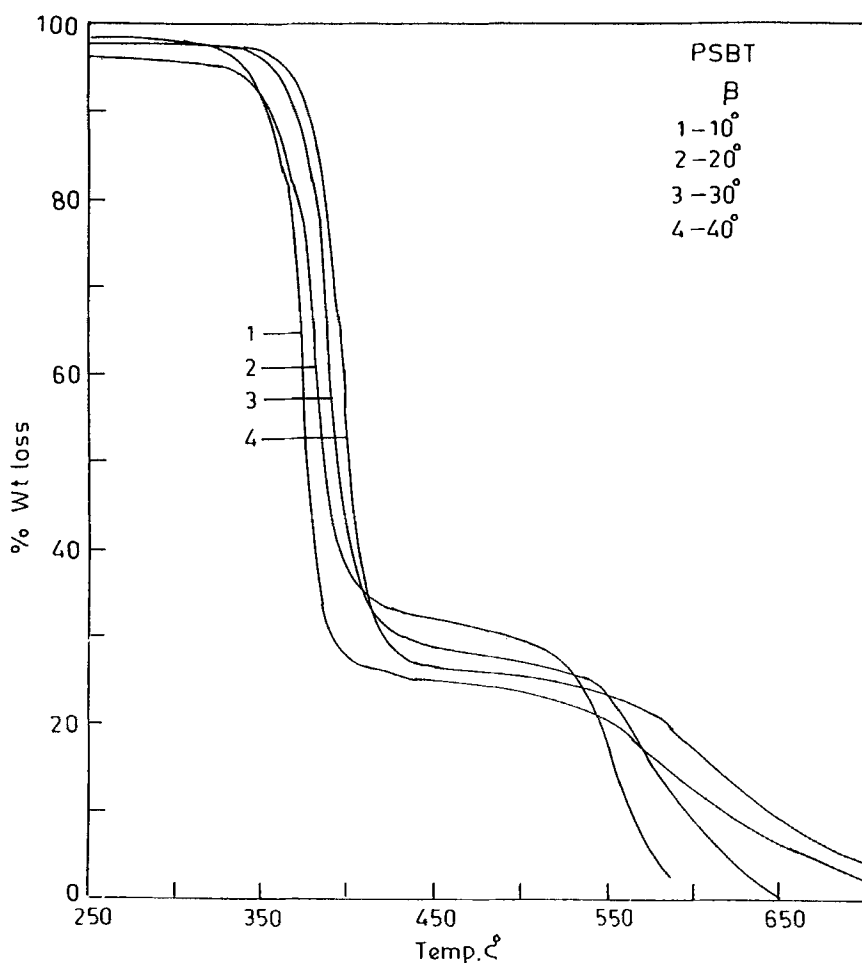

FIG. 4.   TG thermograms of PSBT at four different heating rates in N_2 atmosphere.

TABLE 5. Kinetic Parameters Derived from Thermal Degradation of PSBB and PSBT at Four Different Heating Rates (10, 20, 30, and 40°C/min) in Air[a,b]

| Degree of fractional change "C" | E_a, kcal·mol^{-1} | | | | | |
| | PSBB | | | PSBT | | |
	Anderson [24]	Ozawa [25]	Friedman [26]	Anderson	Ozawa	Friedman
0.1	35.0	33.2	32.7	40.2	38.3	38.1
0.2	43.3	41.3	41.4	48.2	45.6	45.9
0.3	49.3	47.0	47.0	—	—	—
0.4	49.8	47.3	47.4	49.0	46.5	46.6
0.5	49.4	47.1	47.3	56.0	53.2	53.6
0.6	47.5	45.0	45.3	47.2	44.8	45.0
0.65	—	—	—	44.5	42.5	42.3
0.85	22.4	21.5	20.2	17.9	16.9	16.6
0.9	17.9	16.9	15.6	13.8	13.1	10.9
0.95	12.8	12.2	10.3	9.7	9.2	7.2

[a]Frequency factor for Step I. PSBB: $A = 3.42 \times 10^{15}$ min^{-1}. PSBT: $A = 5.76 \times 10^{17}$ min^{-1}.

[b]Apparent order of degradation. PSBB: $n = 0.7$. PSBT: $n = 0.4$.

CONCLUSION

PSBB and PSBT possess good electrical, mechanical, and thermal properties, easy processibility, and excellent solubility in common solvents and chemical resistance. These properties signify the usefulness of these polymers as dielectrics and insulating materials.

ACKNOWLEDGMENTS

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