β-CYCLODEXTRIN REGULATED STEREOREGULARITY AND MOLECULAR WEIGHT IN INCLUSION POLYMERIZATION OF ACRYLONITRILE

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ABSTRACT

Polyacrylonitrile (PAN) polymers were prepared by inclusion polymerization of the monomer using various molar equivalents of β-cyclodextrin (β-CD). Stereoregular (isotactic, atactic and syndiotactic) distributions of the prepared PAN polymers were determined from terminal model Bernoullian statistics using ^{13}C-NMR data. With an increase in acrylonitrile (AN): β-CD ratios, the proportion of isotactic polymers increased. Also, T_g increased along with degradation temperature at higher AN: β-CD ratios. However, molecular weight of the polymers prepared was lower at an AN: β-CD ratio of 10:1, but was found to be larger than the control at an AN: β-CD ratio of 20:1.

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INTRODUCTION

Synthesis of polymers with defined stereoregularity and controlled molecular weights are of great importance to polymer chemists, as the polymer properties are dependent on them. Generally, Ziegler-Natta catalysts [1] or other coordinating initiators [2] are employed for the preparation of stereoregular polymers. Currently, inclusion polymerization is the emerging technique in the field of synthesis of stereoregular polymers.

Polymerization of AN under various conditions has resulted in polymers of divergent stereoregularities [3]. The proportions of syndiotactic, isotactic and atactic polymers formed vary drastically depending on the method of preparation, temperature, catalysts and irradiation [4-7].

Clathrates are defined as crystalline lattices in which the guest monomers occupy the cavities, tunnels or channels of the host lattice [8]. Such an inclusion formation affects the propagation step of the polymer reaction, leading to polymers with controlled stereoregularity [9, 10] and molecular weights.

Various host molecules have been used for the preparation of stereoregular or stereo-controlled polymers. A stereoregular rich polyacrylonitrile with 70-85%, isotacticity, along with small amount of syndiotactic configuration was prepared by γ-irradiation [11] of AN monomer inside the urea-canal system in the solid state. This stereoregularity was also controlled by changing the AN-urea molar ratio, reaction temperature and time. Also, a very high stereoregular polyacrylonitrile polymer was prepared by polymerization of AN monomer within a *tris*-(o-phenylenedioxy)cyclotriphosphazene tunnel [12].

Although, numerous studies have been dedicated to inclusion polymerization using several host molecules [13-15], less attention has been paid to the unimolecular host, β-cyclodextrin (β-CD. β-cyclodextrin was used for the first time in the field of inclusion polymerization by Maceijewskie *et al.* [16]. The present study describes the results from the work on inclusion polymerization of acrylonitrile using -cyclodextrin.

RESULTS AND DISCUSSION

The viscosity average molecular weights of the PAN polymers prepared are given in Table 1. In the presence of 10:1 AN:β-CD the molecular weight of the polymer decreased, which, however showed a molecular weight greater than the control at 20:1 AN:β-CD ratio.

TABLE 1. Viscosity Average Molecular Weights of PAN Polymers[a]

Molar ratio of AN: β-CD	Viscosity Average Molecular Weights
Control	3.41×10^5
10 : 1	9.15×10^4
20 : 1	4.69×10^5

[a] Error range for determining viscosity average molecular weight will be in the range 5%.

The stereoregularity of polyacrylonitrile polymers prepared were investigated by ^{1}H-NMR spectroscopy [17]. The tacticity of the polymers prepared were evaluated using β-CH_2 protons resonance according to the method of Yamadera and Murano [18] and the results obtained in this study are shown in Table 2. Polymerization carried out in the absence of β-CD gave 54% isotactic and 46% syndiotactic polymers. When the molar ratio of AN to β-CD was 5:1, the proportions of isotactic and syndiotactic polymers formed were 59 and 41%, respectively. However, when the molar ratios were increased to 10:1 and 20:1, the isotactic to syndiotactic ratios were found to be 64:36 and 68:32, respectively. Thus, an increase in the AN:β-CD ratio caused an increase in the proportion of isotactic polymers formed.

TABLE 2. -CD-Mediated Stereoregularity in PAN Polymerization[a]

AN: β-CD	Ratio of Isomers (%)	
Molar Ratio	Isotactic	Syndiotactic
1 : 0	54	46
5 : 1	59	41
10 : 1	64	36
20 : 1	68	32

[a] Chemical shift values of the six peaks used in the evaluation for calculating the ratio of isomers are 2.06, 2.10, 2.12, 2.16, and 2.19 ppm. Line width values for the -CH_2 peaks for the four polymers mentioned above are 0.034, 0.347, 0.038, and 0.033 Hz, respectively. The error in measurements will be ± 5%. The values are the average of two samples for the same AN:β-CD molar ratio.

In the present work, the tacticity distribution of the PAN polymers were evaluated from ^{13}C-NMR spectra (Figure 1). The triad tacticities of the polymers prepared were analyzed using nitrile carbon signals in the region 119.1- 119.9 ppm [19]. They consisted of three main peaks, corresponding to three possible steric triad configurations. The peak at 119.9 ppm corresponded to isotactic (mm), the peak at 119.7 ppm corresponded to atactic or heterotactic (mr), and the peak at 119.1 ppm corresponded to syndiotactic triads (rr) [20]. The splittings observed in the three major peaks might be due to undefined tetrad or pentad sequences or due to noise level of the spectrum. The areas of the three peaks were determined by cut and weigh method [21, 22].

The tacticities of the polymers were determined using triad peak intensity data and they were found to conform to Bernoullian statistics (terminal model) [23, 24].

This model requires a terminal dyad and triad fractions totaling to unity by definition:

$$(m) + (r) = 1 \quad \text{and} \qquad (m) = (mm) + 0.5\,(mr)$$
$$(mm) + (rr) + (mr) = 1 \qquad (r) = (rr) + 0.5\,(mr)$$

where m=meso and r=racemic.

The probability of isotactic, atactic and syndiotactic triad formation can be shown as:

$$(mm) = (m)\,(m) = P_m^2$$
$$(mr) = 2\,(m)\,(r) = 2P_m(1-P_m)$$
$$(rr) = (r)\,(r) = 2(1-P_m)^2$$

Table 3 shows both the calculated and experimentally observed values for all the polymers prepared and also the proportions of isotactic and syndiotactic polymers obtained from these values. The data clearly show that the observed NMR peak areas obey Bernoullian statistics at the triad sequence level without involving the need for the use of tetrad and pentad sequences in the testing procedures. The data was also found to fit quite well to the Bernoullian testing model for the triad sequence [25] of the type

$$4\,(mm)\,(rr)\,/\,(mr)^2 = 1$$

Except for the control, the isotactic to syndiotactic ratios determined from ^{13}C-NMR data were similar to those observed from ^{1}H-NMR studies. ^{1}H-NMR data had a drawback in that it could not resolve atactic proportions clear-
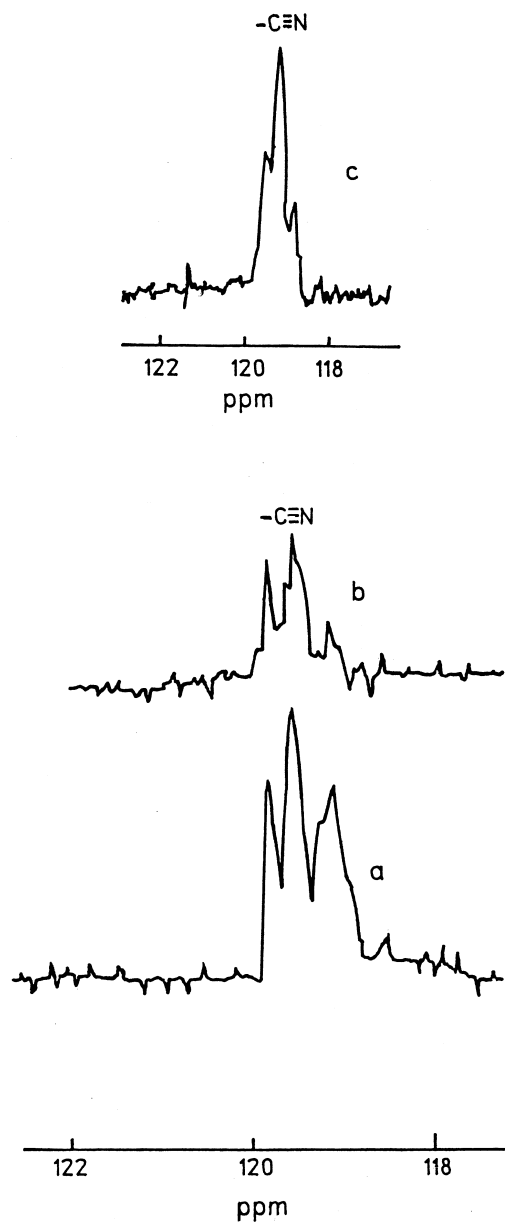
Figure 1. ^{13}C-NMR spectra of PAN polymers. Expanded region of nitrile carbon region from 118.0-122.0 ppm. (a and b) recorded on a 40 MHz instrument; (c) recorded on a 67.5 MHz instrument; (a) - polymer prepared without β-CD; (b) - Polymer with 10:1 AN: β-CD; (c) - Polymer with 20:1 AN:β-CD. About 3000-4000 scans were accumulated. A delay of 3 seconds was employed between pulses. A 20% W/V solution of PAN polymers in DMSO-d^6 was employed.

TABLE 3.   Stereoregularity of the PAN Polymers Calculated by ^{13}C-NMR Spectra[b]

AN:β-CD molar ratio	P_m	Ratio of Triad Concentration[a]			Ratio of Isotactic to Syndiotactic	
		mm	mr	rr	Isotactic[c]	Syndiotactic[c]
1:0	0.397	0.158 (0.206)[d]	0.479 (0.382)	0.364 (0.412)	30 (33)	70 (67)
10:1	0.555	0.308 (0.333)	0.49 (0.444)	0.197 (0.2220)	61 (60)	39 (40)
20:1	0.563	0.32 (0.131)	0.49 (0.613)	0.19 (0.2560)	63 (66)	37 (34)

[a]Triad concentrations evaluated by Bernoullian statistics model.
[b]Error in tacticity values are 5%.
[c]For evaluating isotactic and syndiotactic proportions mm and rr alone were considered, mr values which correspond to atactic were ignored.
[d]Values in bracket correspond to ratio of areas of the peaks obtained directly from ^{13}C-NMR spectra.

ly. In this respect, ^{13}C-NMR data were quite informative. This would explain the observed slight difference between the actual proportions of isotactic and syndiotactic polymers obtained from ^{1}H and ^{13}C-NMR data.

Here also, with increase in β-CD concentrations, isotactic proportions increased similar to those observed from ^{1}H-NMR data. ^{13}C-NMR studies have also shown that the atactic content was not altered significantly in the control polymer and that obtained in the presence of β-CD. Only the isotactic and syndiotactic proportions varied significantly.

Differential Scanning Calorimetry of PAN Polymers

The thermal behavior of the polymers prepared by inclusion polymerization was investigated by Differential scanning calorimatry (DSC). The thermograms of the PAN polymers prepared are shown in Figure 2. The control gave a glass transition temperature of (T_g) 91.4°C, which matched with the reported value (around 97°C) for acrylonitrile polymers [26]. With decrease in β-CD proportion, T_g was found to increase only very slightly from 108.0°C for 10:1 AN:β-CD to 108.4°C for 20:1 AN:β-CD.
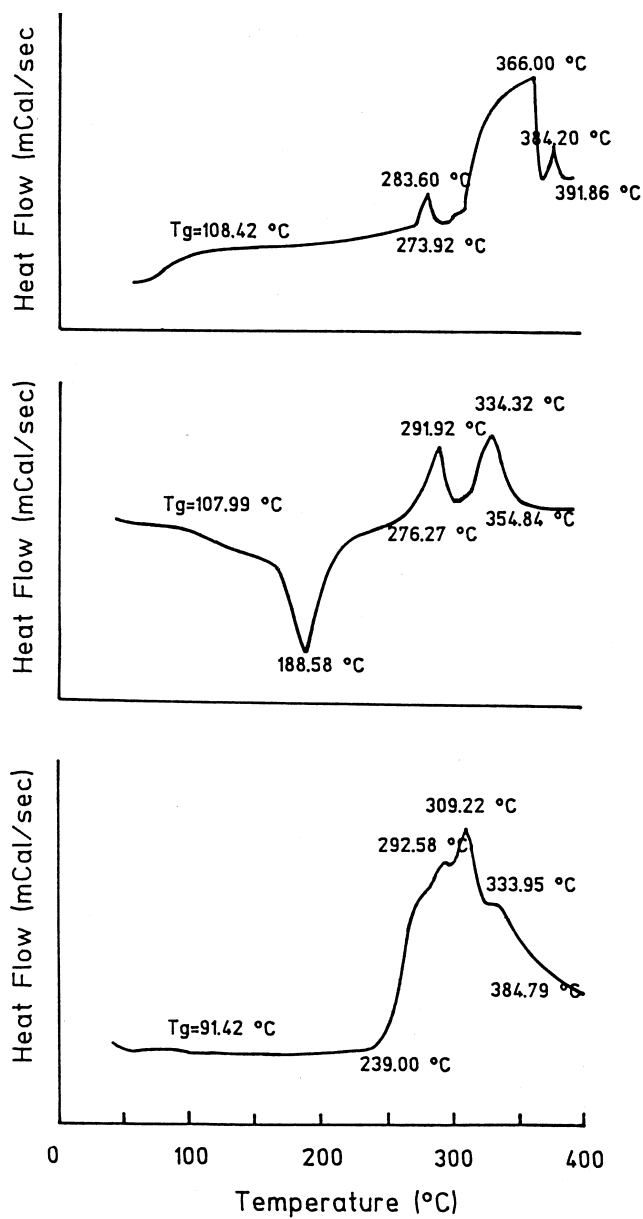
Figure 2. DSC thermograms of PAN polymers. Lower trace: polymer prepared in the absence of β-CD; Middle trace: polymer prepared with 10:1AN:β-CD; Upper trace: polymer prepared with 20:1AN:β-CD. A heating rate of 20C/min was employed for all the polymers.

Polyacrylonitrile polymers do not give endothermic peaks since they do not exhibit definite melting [27]. The polymers begin to degrade on heating between 250 and 300°C, usually accompanied by evolution of gases due to cyclization [28] such as HCN, NH_3, and N_2, resulting in the formation of an exothermic peak [29]. In this study, the degradation began at 230.0°C and extended upto 384.8°C, showing two to three peaks. The thermal behavior of the control polymer was not very much different from that of the polymer prepared with -CD, but, with slight increase in exothermic temperatures in the initial as well as in the final stages of decomposition. However, certain anomalies like an endothermic peak at 188.6°C in case 10:1 AN:β-CD polymer were observed for which a satisfactory explanation cannot be given presently.

These studies have clearly indicated the greater stability of the polymers prepared in the presence of β-CD when compared to the control. For example, the exothermic emission began at about 30°C higher temperature for the 10:1 and 20:1 polymers than the control. Similar behavior was also observed in case of T_g of the prepared polymer, where 10:1 and 20:1 AN:β-CD polymer showed a higher T_g of about 16 to 17°C than the control.

The rate of polymerization in the presence of β-CD was found to be slower than that of the control. The molecular weight built-up of the polymers was also slow. Since all the reactions were carried out for the same duration, high molecular weights detected for the polymer prepared at 20:1 AN:β-CD ratio might be due to β-CD facilitated link up of terminal monomer groups of long polymer chains. Although the molecular weights of the 10:1 AN:β-CD polymer prepared was less than those of both the control and 20:1 AN:β-CD polymer, the T_g of the same was higher than the control indicating that the increase in T_g was not due to difference in the molecular weight (Table 2). The higher isotactic content observed in case of 10:1 AN: β-CD and 20:1 AN: β-CD polymer should be responsible for the increase in T_g, as it facilitated packing of polymer chains in one plane efficiently. The presence of highly polar groups arranged on the same side of the polymer chains enhance the van der Waal's and other intermolecular forces which hold the chain closer strongly [30]. The enhancement in T_g contributed by the increase in isotacticity resulted in drastic reduction of free volume. Presence of few molecules of trapped along the chain length during polymerization might also be responsible to a lesser extent for holding the molecules together through hydrogen bonding interactions between the nitrile and β-CD hydroxyl groups. Such interaction might also reduce the segmental motions of the polymer chain which occurred during compact packing of the same.

The results obtained from the present study have clearly indicated that presence of β-CD during polymerization affects molecular weights of the polymer chains and their stereoregularities. Needlesstosay, the observed results are due to geometry of orientation of the monomer molecule inside the β-CD cavity during polymerization. The orientation of AN molecule inside β-CD cavity in a 1:1 complex is shown in Figure 3 [17]. Because of the linear nature of the side chain nitrile group being present at an angle of 120° to the linear axis of the double bond, inclusion of the whole molecule inside the β-CD cavity is not possible. This partial inclusion can occur in two ways. Between the orientation of the $=CH_2$ and that of the =CH-C≡N group inside the β-CD cavity, the latter orientation may be preferred due to partial hydrophobicity of the =CH-CN and that of the interior of the β-CD cavity. Such orientation imposes restriction on the extent of the polymerization and increases the residency period of the molecule or radical inside the β-CD cavity, which may favor chain termination abruptly. It is known that the residency time of the monomer on inclusion inside the β-CD cavity is enhanced [31]. Thus, higher concentration of β-CD (such as 5:1 AN: β-CD), which contains about one β-CD molecule for every five molecules of AN, lead to enhanced residency period for AN leading to the formation of low molecular weight polymer chains due to abrupt termination. Conversely, lower catalytic concentrations of β-CD at 10:1 and 20:1 AN: β-CD do not enhance the
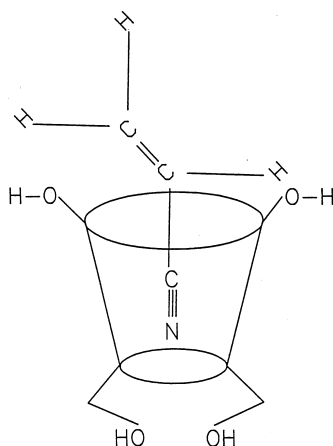
Figure 3.   Inclusion of acrylonitrile monomer inside the Figure 2 β-CD cavity.

residency period of the monomer significantly and hence do not result in abrupt chain termination leading to the formation of higher molecular weight polymer chains. In fact, at 20:1 AN: β-CD ratio, the molecular weight of the polymer formed is greater than that of the control.

During propagation of the polymer chains, high concentrations of β-CD should restrict orientation of bulky nitrile side groups (included inside β-CD) on the same side favoring syndiotactic orientation. But, isotacticity is favored at lower β-CD concentrations as the planar Sp^2 carbon of the monomer in the AN: β-CD complex converts to the Sp^3 carbon of the zig-zag polymer during propagation, throwing the β-CD molecule containing the included =CH-C≡N group on one side, which may orient the incoming =CH-C≡N group on same side due to hydrogen bonding interaction between the β-CD units.

Though the exact role of rotaxane on the control of stereoregularity as well as on the molecular weight is not clear, its formation is reported in several polymerization processes. Even in the present study, less intense β-CD ^1H signals (Figures 4 and 5) from the polymer in DMSO-d_6 were detected. However, it was not possible to find out the number of β-CD molecules which were present adhering to the polymer chain.

These studies have clearly shown the regulatory nature of β-CD in the polymerization process through inclusion of the guest monomer.

EXPERIMENTAL

Chemicals

Acrylonitrile monomer, ammonium persulphate and sodium metabisulfite were purchased from S. D. Fine Chemicals, India. Acrylonitrile monomer was purified over calcium carbonate and sulphuric acid to remove impurities.

Preparation of the Polymer

A typical procedure employed for the inclusion polymerization was as follows. A mixture of appropriate concentrations of 0.05-0.2 mole acrylonitrile and β-CD (host depending on the molar ratio) was stirred in 25-50 ml of water for half an hour to form an inclusion complex. Sodium metabisulphite (20-40 mmol), ammonium persulfate (0.25-1.0 mmol) and 0.1 ml of sulphuric acid in water were added and stirred at 35-40°C under N_2 atmosphere for a period of 4-10 hours. The polymer obtained was then treated with hot water (100 ml) and
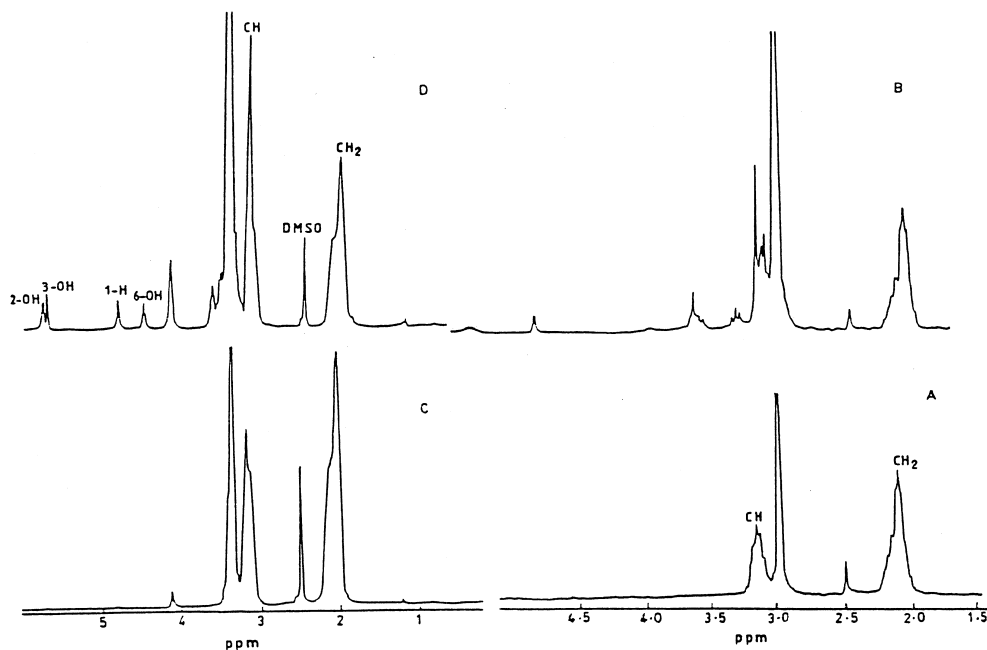
Figure 4. ^{1}H-NMR spectra of PAN polymers prepared in the presence and in the absence of β-CD spectra recorded on the 400 MHz instrument (C and D) at room temperature; (A and B): Spectra recorded on the 270 MHz instrument at 100C. (A and C): without β-CD; (B and D): with β-CD (AN:-CD 10:1). About 200 scans were recorded in DMSO-d_6.

filtered. After several washings with hot water and methanol (50 ml), the residue was dried and weighed [32].

Viscosity Average Molecular Weight

Viscosity average molecular weights (M_v) of the polyacrylonitrile polymers were determined using an Ostwald viscometer at room temperature. Four different concentrations were used for each polymer with at least three efflux times recorded at each concentration. Dimethyl formamide was used as a solvent for viscosity measurements. For each polymer, intrinsic viscosity was calculated from which the molecular weights of the PAN polymers were calculated using Mark-Houwink equation:
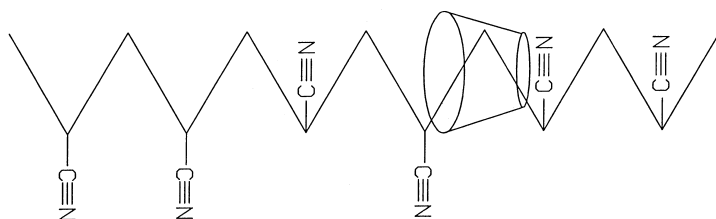
Figure 5.   Rotaxane formation involving β-CD and PAN polymer chain.

$$(\eta) = K \cdot \overline{M}_v^a$$

K and a values are 20.9 x 10^3 ml/g and 0.75, respectively [33] which are constants for polyacrylonitrile in DMF.

Spectroscopy

^{1}H-NMR spectra were recorded on Brüker AMX 400 and WH 270 MHz NMR instruments, each fitted with a Spectrospin magnet operating at 20°C and an Aspect 2000 computer. About 200 scans were collected for each spectrum and all the samples were prepared in DMSO-d_6 and D_2O.

^{13}C-NMR spectra were recorded on the above mentioned NMR instruments which operated at 67.5 MHz and 40 MHz for carbon-13 respectively. About 3000 scans were accumulated for each spectrum and all the samples were prepared in DMSO-d_6. The signals were referenced to DMSO-d_6 at 45.4 ppm to within ± 0.1. Proton noise decoupled spectra were obtained. A delay between pulses of 3 s was employed.

Differential Scanning Calorimetry

Differential scanning calorimetric studies were carried out on Rheometric Scientific, U.K. (DSC PLUS) supported with version 5.42 Software calibrated against Indium, tin, and lead. The polymers used weighed approximately 1 to 10 mg and the equipment operated in the temperature range 30 to 400°C with a 0.01 m.cal/s sensitivity.

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