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Highly Reactive 2,5-Disubstituted Styrene-Based Monomer Polymerized via Stable Free Radical Polymerization: Effect of Substitution and Liquid Crystallinity on Polymerization

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ABSTRACT: The stable free radical polymerization (SFRP) of a liquid crystalline monomer 2,5-bis[(4-butylbenzoyl)oxy]styrene, BBOS, was investigated. BBOS is a substituted styrenic monomer, which polymerizes an order of magnitude faster than styrene under identical bulk polymerization conditions. A comparative study of the polymerization behavior in bulk and solution for BBOS and a model compound was undertaken to elucidate the effect of both electron-withdrawing substituents and liquid crystallinity of the monomer on the polymerization kinetics. Molecular simulation was used to identify a non-LC model monomer, 2,5-diacetoxystyrene (DAS). DAS was polymerized by stable free radical polymerization both in bulk and in solution. In all cases narrow molecular weight distribution (<1.4) was obtained. In bulk, DAS polymerized significantly slower than BBOS, whereas in a dilute solution, the rate of polymerization was quite similar. In-situ X-ray studies carried out during polymerization of BBOS in the neat monomer indicate the presence of a nematic phase which could lead to localized ordering of the monomers during polymerization. In comparison, DAS was found to be more reactive than styrene, because of the electronic effect of the acetoxy groups. However, *p*-acetoxystyrene (PAS) was found to have almost the same observed rate of polymerization as DAS, indicating that steric factors also play an important role in O-substituted compounds.

Introduction

Stable free radical polymerization (SFRP) has been recognized as an important new form of living polymerization, mainly because of the versatility it offers in terms of the broad range of monomers that one can work with. In the field of nitroxide-mediated controlled free radical polymerization, Georges et al.[1,2] developed a bimolecular initiating system, based on 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) in combination with benzoyl peroxide to achieve controlled molecular weight polymers for styrenics and acrylics. The synthesis of new functionalized unimolecular initiators has also expanded the useful temperature range for nitroxide-mediated SFRP from 90 to 135 °C.[3] This technique has been successfully applied to producing macromolecular architectures such as star and graft polymers.[4] Unlike living cationic or living anionic polymerization, living free radical polymerization is tolerant to a number of functional groups.[5,6]

This characteristic of the polymerization makes it especially attractive for the synthesis of controlled molecular weight polymers to provide better insights into structure−property relationships. For example, side group LC poly(methacrylate)s have been synthesized by GTP[7,8] and living anionic polymerization[9] with varying degrees of success, because of functional group complications. Living ring-opening metathesis polymerization (ROMP) of laterally attached mesogenic norbornene monomers have been studied by Pugh et al.[10] More recently, controlled free radical polymerization has been successfully applied to side group, styrenic LC monomers.[11] In LC monomers, the polymerization kinetics may be complicated by the preordering or self-assembly of the monomers. This preordering effect has been reported for styrene and methacrylates with bulky dendritic side groups by Percec et al.[12]

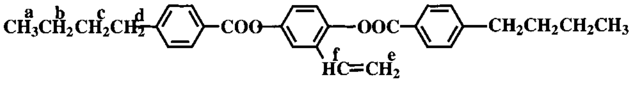

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Figure 1. Structure of [4-butylbenzoyloxy]styrene (BBOS) (**1**).

We have recently studied the synthesis via SFRP of the mesogen jacketed liquid crystalline polymer, poly(2,5-[(4-butylbenzoyl)oxy]styrene], PBBOS, by polymerizing 2,5-(4-butylbenzoyl)oxystyrene, BBOS (**1**), with 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-ethane (**2**) (also known as unimer, refer to Figure 2), as initiator.[13] This monomer is based on vinylhydroquinone and was first synthesized and polymerized by Zhou et al.[14] by conventional free radical polymerization. PBBOS falls into a very distinct class of LC polymers, referred to as “mesogen-jacketed liquid crystalline polymer”.[15] The bulky mesogenic groups are attached without spacer to the polymer backbone in a lateral fashion. Because of the bulkiness and the rigidity of the mesogenic groups surrounding the main chain, it is forced into an extended conformation. This results in stiffening of the backbone and leads to a polymer that behaves like a semirigid main chain liquid crystalline polymer.

The use of controlled free radical polymerization to synthesize mesogen jacketed LC polymer,[13] PBBOS, opens up interesting possibilities to make new rod−coil blocks,[18] triblocks, and star block copolymers. Our earlier studies on the polymerization behavior of BBOS under SFRP conditions indicated an unusually high reactivity compared to those of other styrenics. These interesting observations prompted us to further study the effect of possible preordering of monomers on the

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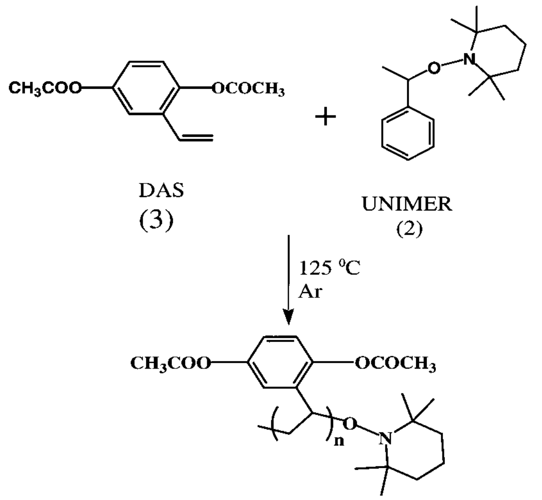


Figure 2. Scheme of synthesis of poly(2,5-diacetoxystyrene) by reaction of 2,5-diacetoxystyrene (DAS) (**3**) with unimer (**2**) at 118 °C in inert atmosphere.

reaction mechanism. In this paper we also report the SFRP synthesis of a non-LC model polymer poly(2,5-diacetoxy)styrene, PDAS (Figure 1), along with its polymerization behavior as compared to PBBOS in both solution and bulk. DAS was chosen as a model compound because it has similar electronic structure to BBOS as indicated by molecular simulations.

Experimental Part

Synthesis of the Model Compound DAS. The monomer 2,5-di-acetoxystyrene, DAS (Figure 2), was synthesized starting from 2-vinyl-1,4-dihydroxybenzene and acetic anhydride in the presence of a catalytic amount of concentrated sulfuric acid, according to the procedure described by Cassidy et al.[16] The purification procedure was modified. It was found that recrystallization alone does not give a product with high enough purity to carry out SFRP. Therefore, column chromatography was performed using a 3:2 ratio of diethyl ether: petroleum ether to ensure removal of any traces of vinylhydroquinone. The resulting white solid was subsequently recrystallized twice from absolute ethanol. White crystals were obtained with a mp of 52 °C, which is 4 °C higher than that reported by Cassidy et al.

^{1}H NMR (CDCl$_3$): $\delta = 2.06-2.91$ (d), 6H for OCOCH$^a_3$, 5.41−5.82, 2H for =CH$^b_2$, 6.72−7.04, 1H for −CH^c= and 7.12−7.91, 3H for the phenylene ring.

^{13}C NMR (CDCl$_3$): δ 20.95, 21.20, 117.36, 119.32, 121.88, 123.60, 129.81, 131.43, 145.44, 148.50, 169.26, 169.43.

Synthesis of BBOS. The monomer 2,5-bis[(4-butylbenzoyl)-oxy]styrene, BBOS (Figure 1), was synthesized by the reaction of 2-vinyl-1,4-dihydroxybenzene and 4-butylbenzoyl chloride according to the method described by Zhou et al.[14]

^{1}H NMR (CDCl$_3$): $\delta = 0.95$, 6H for CH$^a_3$,1.35, 4H for CH$_2^b$,1.65, 4H for CH$_2^c$, 2.70, 4H for CH$^d_2$, 5.10−5.90, 2H for =CH$^e_2$, 6.60−6.95, 1H for −CH^f= and 7.00−8.30, 11H for the phenylene rings.

As reported earlier,[14] BBOS possesses a smectic phase between its melting temperature of 68 °C and clearing temperature of 95 °C.

Polymerization. Polymerizations were carried out both in bulk and in solution. Bulk polymerization of BBOS was carried out with unimer, as described by Pragliola et al.[13] DAS was also polymerized in bulk at both 118 and 125 °C, using a 1000/3 ratio of DAS/unimer. Monomer was mixed with initiator in a small glass tube containing a stir bar and purged with inert gas for 15 min. This was vacuum-sealed and premixed in a water bath at 55 °C for 3 min, followed by complete immersion of the tube into an oil bath at the required temperature. DAS has a tendency to sublime at the polymerization temperature; hence, it is necessary to immerse the entire tube into the oil bath at the set temperature for reliable results.

Solution polymerizations were carried out at 125 °C, using a 1.5 M solution of the monomer in *o*-dichlorobenzene at a 1000:3 ratio of monomer:unimer. Reaction times between 0.5 and 24 h were used for bulk polymerization and between 2 and 53 h for solution polymerization. PDAS is soluble in hot aromatic solvents but tends to form a separate layer in cold aromatic solvents.

PDAS has good solubility in acetone, chloroform, and tetrahydrofuran. Following polymerization, PBBOS was precipitated with methanol, while PDAS was precipitated from petroleum ether and dried in a vacuum oven at room temperature.

Characterization. A Varian XL 400 NMR using chloroform-*d* as solvent with tetramethylsilane as internal standard was used to obtain the NMR spectra of all the compounds. Thermal analysis was carried out under a nitrogen atmosphere by means of Perkin-Elmer DSC7 and TGA 7 instruments at a heating rate of 10 °C/min. Measurements of both molecular weight and polydispersity of all polymer sample were carried out using Waters Ultrastyragel HT columns operating at 40 °C. THF was used as the solvent, and the GPC was operated at 1 mL/min. Solution concentrations of 1 mg/mL for PBBOS, 2 mg/mL for PDAS, and solution volumes of 50 μL were employed. Molecular weights were calculated from GPC elution volume data using monodispersed polystyrene standards.

Results and Discussion

Synthesis. As reported in our earlier paper,[13] BBOS can be successfully polymerized in the melt under SFRP conditions using unimer initiator to obtain a sample with low polydispersity. By varying the reaction time, good control of molecular weight can be achieved. It was also observed that BBOS is a very reactive monomer compared to other conventional styrenic monomers when polymerized under SFRP conditions. Typically a conversion of 50% can be attained in less than 4 h without the use of any rate-enhancing additives. In trying to explain the unusually high reactivity of the monomer, we speculated that the liquid crystalline melt phase of BBOS might play a role, combined with the electron-withdrawing character of the benzoate groups. To test this hypothesis further, we prepared a non-LC model compound, 2,5-diacetoxystyrene (DAS). Molecular simulation of DAS and BBOS (using the MACSPARTAN Plus program by Wave Function) was done to evaluate their relative electron density. The semiempirical molecular orbital method, PM3, was used to compare the electron densities on the X−^{1}CH=^{2}CH$_2$ carbons. The electron densities on the ^{1}C and ^{2}C carbons were determined to be −0.007 and −0.169, respectively, for BBOS and −0.018 and −0.212, respectively, for DAS. This indicates that DAS should have very similar reactivity to BBOS based on electronic considerations alone since the diacetoxy groups will have electronic effects nearly identical to the benzoate groups on the vinylhydroquinone. The use of acetoxy groups should also have similar neighboring group participation of the ester functionality on the reactivity. Given these facts, the other major variable that could influence the polymerization reaction kinetics of the two monomers is the liquid crystalline phase of BBOS. The preordering effect can only take place in the melt, i.e., under bulk polymerization conditions, and therefore we would expect the solution polymerization rates of the model compound and BBOS to be similar.

DAS has earlier been polymerized by conventional free radical polymerization, using AIBN in benzene.[16]

Table 1. Bulk Polymerization of DAS at 125 °C (Using a Molar Ratio of DAS/Unimer: 1000:3)

time (h)	M_n	PDI	% conv
2	9 700	1.23	7
4	22 670	1.23	12
8	24 290	1.23	23
12	25 661	1.24	36
19	30 805	1.25	46
24	33 000	1.29	51
29	35 430	1.31	59

We conducted the bulk polymerization of DAS at both 118 and 125 °C, using a 1000:3 ratio of monomer:unimer under SFRP conditions. Table 1 shows the resulting molecular weight, polydispersity, and monomer conversion data for different samples of PDAS, as monitored with time at 125 °C in bulk. For all samples, a narrow molecular weight distribution (1.23−1.31) was obtained. The molecular weight and extent of conversion could be controlled very well by adjusting the reaction time (Figure 3). However, the molecular weight of the resulting polymer does not increase linearly with conversion over the entire reaction; thus, under the conditions used DAS satisfies only some (such as chain extension by sequential polymerization and narrow polydispersity) but not all the conditions of a living polymerization. The DAS conversion was determined by monitoring the integrated intensity of the UV signals of the monomer and the polymer by GPC. Calibration of GPC data with known ratios of monomer and polymer showed an error of 7−10% in the calculated conversion. These data were compared with the data reported for BBOS and styrene under similar conditions[13] (Figure 4). It requires close to 37 and 24 h at 118 and 125 °C, respectively, for DAS to reach 50% conversion compared to 4 h for BBOS at 118 °C. This significant difference in the rate of polymerization of BBOS compared to DAS is apparent from the first-order plot of the bulk polymerization data (Figure 4). As shown in the figure, there is a deviation from linearity at higher conversions, which could be due to other physical effects such as increased viscosity of the medium. The observed rate constant derived from the slope of the above plot is 4.1×10^{-5} S^{-1} for BBOS as compared to 6.0×10^{-6} S^{-1} for DAS at 118 °C. This indicates that BBOS has an order of magnitude higher reactivity than DAS and styrene ($K_{obs} = 3.4 \times 10^{-6}$ S^{-1} at 123 °C). Even though polymerization of BBOS was carried out above the clearing temperature of the monomer, there may be some associated “lining up” of the monomers aiding in more efficient polymerization, whereas no such possibility exists for the nonliquid crystalline monomer, DAS. Since the preordering effect can only take place in the melt, we repeated the polymerization studies in a dilute (1.5 M) solution of monomer in *o*-dichlorobenzene. Table 2 shows the variation of molecular weight, PDI, and percent conversion with time for the solution polymerization of both BBOS and DAS. Use of other polymerization solvents such xylene or toluene gave relatively more polydispersed products than when using *o*-dichlorobenzene.

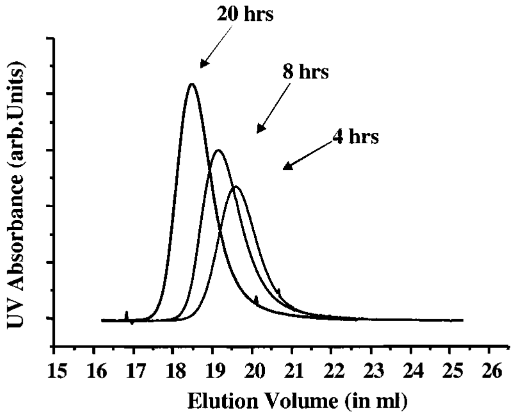


Figure 3. GPC curves showing the progress of polymerization of DAS with unimer at 125 °C with time.

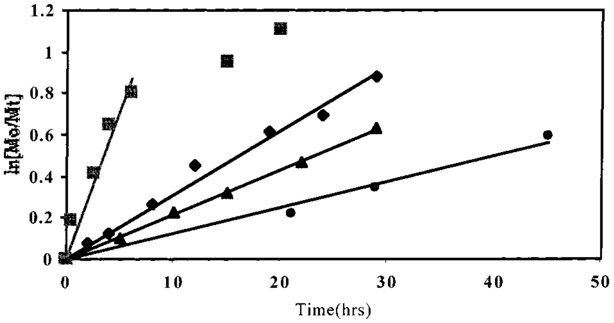


Figure 4. First-order plot of ln[M_0/M_t] vs time (in h) for polystyrene (PS), poly(2,5-bis[(4-butylbenzoyl)oxy]styrene) (PBBOS), and poly([2,5-diacetoxy]styrene) (PDAS) via SFRP conditions. (■) PBBOS (bulk polymerized at 118 °C, see ref 13), (◆) PDAS (bulk polymerized at 125 °C), (▲) PDAS (bulk polymerized at 118 °C), (●) PS (bulk polymerized at 123 °C without any additives, see ref 19).

Table 2. Solution Polymerization of BBOS and DAS at 125 °C, Using 1.5 M Solution in *o*-Dichlorobenzene, with a Monomer:Unimer Ratio of 1000:3

time (h)	M_n	% conv	PDI
	PDAS		
5	12 563	5	1.24
10	19 000	15	1.22
22	21 911	30	1.22
44	22 800	42	1.30
60	23 100	48	1.30
	PBBOS		
2	12 551	10	1.52
6	15 284	18	1.40
11	18 582	25	1.30
22	23 032	35	1.32
45	25 795	45	1.35
60	26 000	55	1.30

This property of *o*-dichlorobenzene leads us to some very interesting observations. Figure 5 shows the data for solution polymerization of BBOS and DAS (1.5 M solution in *o*-dichlorobenzene)at 125 °C. All samples obtained in solution had a narrow molecular weight distribution, typically between 1.54 and 1.3 for PBBOS and 1.2−1.3 for PDAS (Figure 6). The rate of polymerization is quite similar for both monomers in solution. At lower conversions, BBOS has a marginally higher rate of polymerization, and at around 50% conversion this difference narrows. This observation again indicates the substantial contribution of the LC nature of the monomer to the rate of polymerization under bulk polymerization conditions. It should be noted that termination rate constants k_t would play an important role in the observed rate. As studied earlier by Fakuda et al.,[20] at higher conversions the polymer concentration increases and diffusion of the polymer radicals leading to bimolecular termination decreases, thereby causing a higher observed rate. This is also likely to be the case for BBOS, since it is a very bulky monomer and the rate of termination reactions will be substantially lower than a less bulky monomer like DAS. Hence, the observed

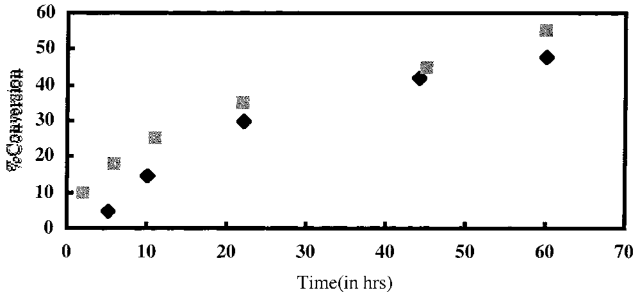


Figure 5. Comparative plot of percent conversion with time for the solution polymerization of BBOS and DAS in a 1.5 M solution of *o*-dichlorobenzene at 125 °C. (■) PBBOS, (◆) PDAS.

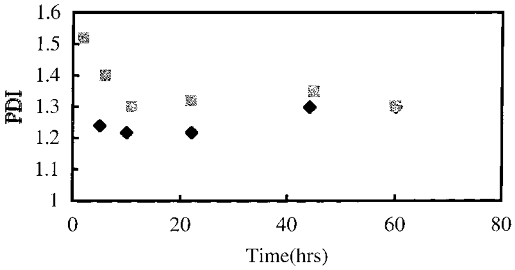
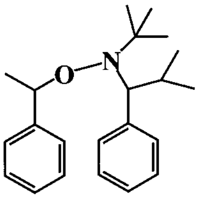


Figure 6. Plot showing the variation of polydispersity (PDI) with time for solution polymerization of BBOS and DAS at 125 °C in *o*-dichlorobenzene. (■) PBBOS, (◆) PDAS.



(4)

Figure 7. Structure of 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane, initiator (**4**).

accelerated rate of polymerization is possibly a combination of reduced termination and contribution of the liquid crystalline melt phase. This has been observed earlier for the photopolymerization of LC acrylate monomers in the LC state.[17]

We also polymerized BBOS in its smectic phase at 90 °C, using 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (**4**) as initiator. This initiator, synthesized by Hawker et al., is capable of initiating the polymerization of styrene at 90 °C.[3] Bulk polymerization of BBOS was carried out using a 1000:3 ratio of monomer:initiator (**4**) (Figure 7). In 2 h the polymerization was more than 98% completed, reaching a molecular weight of 92 000 with a PDI of 2.5. At 90 °C, the thermal polymerization of BBOS should be quite low; hence, the observed accelerated rate of polymerization in the smectic phase is probably due to both the ordering of monomers and higher viscosity in the smectic phase combined with the bulkiness of the mesogen leading to reduced termination rates. On the other hand, polymerization of DAS at 90 °C resulted in just 4% conversion in 2 h, with a PDI of 1.5.

It should also be noted that DAS is a more reactive monomer in bulk as compared to styrene (Figure 4). Typically a molecular weight of 33 000 can be reached in 24 h for DAS at 125 °C. We further examined the rate of polymerization of *p*-acetoxystyrene (PAS) under identical conditions as DAS. At 125 °C, PAS has an observed rate constant of $\sim 8.0 \times 10^{-6}$ S^{-1}, which is very close to the corresponding value of 8.58×10^{-6} S^{-1} for DAS. This seems logical if we consider the Hammett constant (σ) value for acetoxy substitution on an aromatic ring is the same for both meta (0.39) and para (0.31) substituents within an uncertainty range of 0.1.[19] The presence of a second acetoxy group at the ortho position of the reactive site in DAS does not increase the reactivity probably because steric hindrance plays a dominant role.

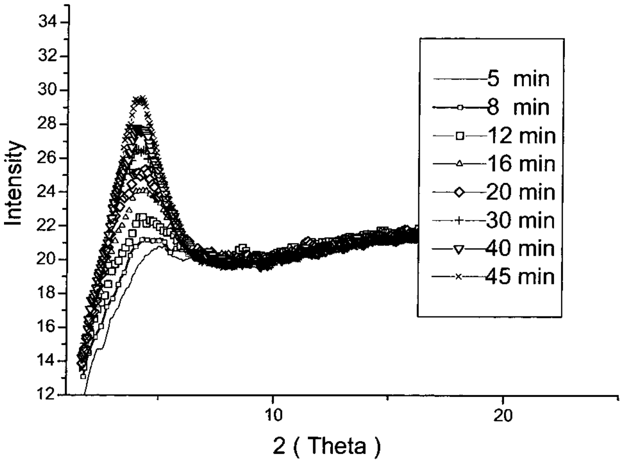


Figure 8. Wide-angle X-ray scattering monitored with time for in-situ polymerization of BBOS with unimer at 118 °C.

Thermal Characterization of the Polymers. Poly(2,5-diacetoxy)styrene, though synthesized earlier by Cassidy et al. by conventional free radical polymerization, has not been characterized in the literature to date. The glass transition temperature of PDAS was determined to be 107 °C by DSC. TGA analysis of the polymer shows PDAS to be stable up to 359 °C. This is comparable to the thermal stability of PBBOS (T_g 130 °C, decomposition temperature 380 °C). Detailed thermal characterization of BBOS and the corresponding polymer PBBOS has been reported in our previous paper.[13]

X-ray Studies and Phase Behavior during Polymerization of BBOS. In-situ X-ray studies were performed to detect the possible presence of a liquid crystalline phase during polymerization. A 1.5 mm X-ray capillary was filled with a premixed sample of monomer and initiator and mounted on a hot stage. The mixture was rapidly heated to 118 °C, and the WAXS behavior was monitored every 2 min. WAXS was carried out on Bruker Discover X-ray diffractometer using Cu bias ($\lambda = 1.54$ Å). As seen from the data shown in Figure 8, a peak between 19 and 20 Å appears in all scans taken from 2 to 60 min of the start of polymerization. After 50 min from the start of the polymerization no significant change in signal intensity was observed. In Figure 8 the absolute intensities observed have been plotted against 2θ values. This corresponds to an interchain packing distance that is close to that observed for fibers drawn from BBOS homopolymer (17.2–18 Å). The polymer is at a temperature (118 °C) below its glass transition temperature (130 °C), but in the monomer swollen, plasticized state it is likely to have a lower T_g with enough mobility for rapid polymerization but hindered termination. One can speculate that the nematic polymer chain may also induce localized ordering of the monomer, leading to further accelerated rate of polymerization. These results should be taken as qualitative because of the difficulty in ensuring a

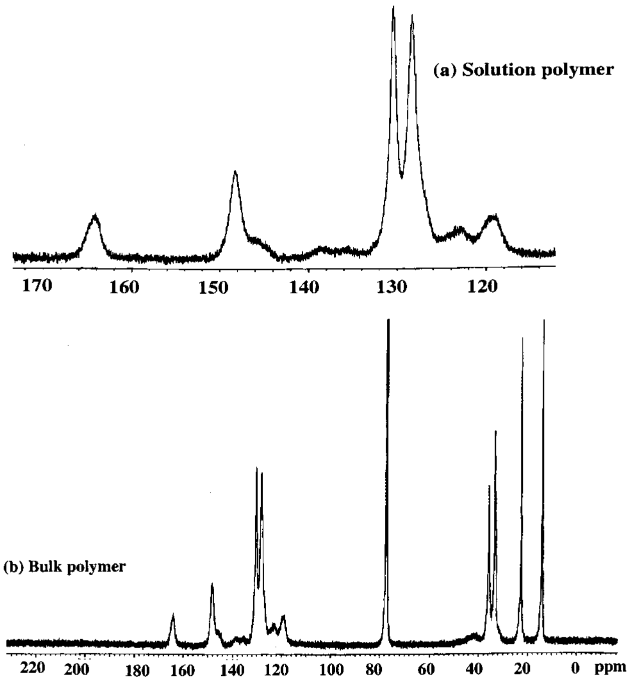


Figure 9. Comparison of ^{13}C NMR (400 MHz) of PBBOS polymerized in (a) solution and (b) bulk.

uniform mixture of monomer and initiator in the absence of stirring (which is not possible in situ). In the capillary tubes used for X-ray diffraction it was also impossible to completely exclude oxygen; hence, the in-situ X-ray studies could not be perfectly correlated to the kinetic studies. However, the clear presence of the LC phase in the BBOS polymerization mixture and the dramatically different behavior for the amorphous DAS polymerization strongly point to the effect of liquid crystallinity on the presence of a mesophase in the formation of PBBOS.

Spectroscopic Characterization. ^{13}C NMR was used to investigate any change in tacticity introduced in the LC polymer, due to the difference in the mechanism between polymerization in bulk and solution. ^{1}H NMR does not allow the determination of the tacticity of the polymer, as it resulted in very broad bands with poor resolution. The signal for main chain α and β carbons show very poor resolution (39−42 ppm). This can be attributed to the low mobility of the main chain, i.e., “the mesogen jacket effect” as earlier reported by Zhou et al.[18] The chemical shift of the quaternary aromatic carbon attached to the α carbon should show a marked dependence on the stereochemical configuration. However, from the ^{13}C NMR, we found that all the aromatic carbons appear at identical chemical shifts for both solution and bulk polymer (Figure 9), indicating no observable difference in the tacticity of the polymers.

Comparative polymerization studies of BBOS with the model compound DAS, in bulk, in both the isotropic and smectic phase regime of the LC monomer further lends support to the concept that localized ordering of the monomer could lead to efficient polymerization. The rates of solution polymerization of DAS and BBOS are quite similar, which is in agreement with the above interpretation. However, this difference in the mechanism of polymerization in bulk and solution for BBOS is not reflected in the tacticity of the polymer, as we did not find any observable difference by NMR. X-ray studies show the presence of a nematic phase during polymerization which could result in localized lining up of the monomer during polymerization. It was also found that *p*-acetoxystyrene has a rate of polymerization similar to that of DAS, indicating that steric factors play a very important role in reactivity. We are currently investigating the structure−morphology relationship for a series of blocks and star blocks of this unique LC monomer with styrene and in most of the cases we observed nanosphere formation. This observation is consistent with diblock copolymers of mesogen jacketed polymers with styrene that have also been synthesized and studied recently by Zhou et al., by the dynamic light scattering technique.[21] We expect that these studies will provide new insight into the polymer formation process.

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