Optimization of the Polymerization Process of Sulfinyl Precursor Polymers toward Poly(*p*-phenylenevinylene)

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ABSTRACT: The prerequisites for the polymerization process of sulfinyl monomers toward precursor polymers for poly(*p*-phenylenevinylene) were investigated. In this process, proton abstraction affords the premonomer anion, which is converted to the actual monomer, viz. a *p*-xylylene derivative. These *p*-xylylene derivatives polymerize spontaneously without external initiation. In hydrogen bond donor solvents (HBD solvents) like alcohols, three products can be isolated. High molecular weight polymer is formed together with a residual fraction that consists of a minor amount of premonomer and a large amount of solvent-substituted product. These solvent-substituted products are most likely formed by addition of a solvent anion to the actual monomer and cannot participate in the polymerization process anymore. Solvent substitution is therefore an important side reaction and has to be avoided. It was found that, in branched alcohols such as *s*-butanol, conversion of premonomer to actual monomer is very efficient, resulting in a rapid buildup of *p*-xylylene derivative. In this way the polymer yield was increased to 90%.

Introduction

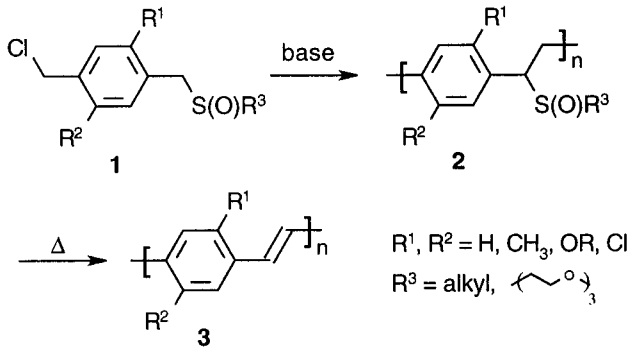
Light-emitting diodes (LEDs) in which thin films of conjugated polymers constitute the active layer were first reported in 1990 by Friend et al.[1] They succeeded in fabricating a LED with poly(*p*-phenylenevinylene), PPV, as the emission layer. Interest in this field then grew rapidly, and extensive research was performed in order to improve the synthesis of the active materials and the performance of these devices.[2]

Precursor routes for conjugated materials are of major importance for the development of optical and electronic applications for organic semiconductors. They introduce processability, which makes the incorporation of these materials into devices feasible. A precursor route that has shown to be very versatile is the one introduced by Wessling and Zimmerman[3,4] and optimized by other groups.[5−7] Galvin et al.[8] favored a xanthate precursor polymer soluble in organic solvents and claimed that it gave higher device efficiencies than the Wessling route. For both these precursor routes easily accessible, symmetrical monomers are used. The main drawback, however, is that the same functional groups (sulfonium or xanthate) have to function both as a polarizer and as a leaving group. This means that a compromise of properties is inevitable. Therefore, these precursor routes do not offer a broad range of synthetic possibilities to tune the polymerization process.

To have control over the polymerization process[9,10] and the stability of the precursor polymers **2**,[11] an unsymmetrically substituted sulfinyl monomer like **1** is used (Scheme 1), in which a differentation is made between leaving group (Cl) and polarizer (S(O)R). In contrast to the Wessling route, this route is also applicable for monomers with extended aromatic systems such as 2,6-naphthalene or 4,4′-biphenylene.[10]

By changing the R group of the nonionic polarizer, the solubility of both the monomers and the precursor polymers can be altered. This means not only that characterization of the precursor polymer and determination of molecular weight and molecular weight distribution can be performed in a straightforward manner but also that for processing of these materials a broad range of solvents becomes available. Moreover, the polymerization itself can be investigated in various different solvents. This gives us ample opportunity to tune the reaction conditions and to define the prerequisites for an efficient polymerization process.

Scheme 1. General Scheme of the Sulfinyl Precursor Route



In this paper a detailed investigation of the polymerization of sulfinyl monomers in different solvents is presented.

Results and Discussion

Monomer Synthesis. In the sulfinyl precursor route a chemical differentiation is made between leaving group and polarizer. As a consequence, an unsymmetrically substituted monomer like **1** has to be used. A highly selective route for producing these unsymmetrically substituted monomers will be published elsewhere.[12] The crucial step in this route is introduction of a thioether group by reaction of a symmetrical bis-sulfonium salt **4** with a thiolate anion to give the unsymmetrical product **5** (Scheme 2). Azeotropical removal

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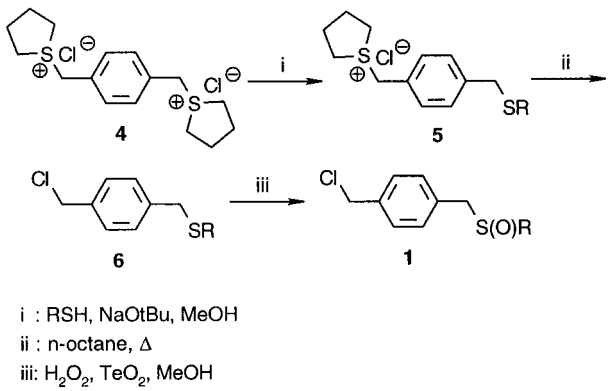
Scheme 2. Monomer Synthesis



of tetrahydrothiophene affords thioether **6**, which can be selectively oxidized to sulfinyl monomer **1**.

Polymerization. Polymerization of these unsymmetrical sulfinyl monomers is a complicated process, in which different steps can be distinguished (Scheme 3). These different steps are linked together, making it difficult to assign for instance an increase in polymer yield to a single changed reaction parameter. It is beyond the scope of this paper to elucidate all these different steps in detail. The results of different reaction conditions will be discussed as a function of changes in polymer yield and yield and composition of the low molecular weight fraction.

To investigate the base-induced polymerization reaction in different solvents, two monomers with a broad solubility range, **1f** and **1g**, were used. The base of choice was NaO*t*-Bu unless stated otherwise. This base was added in an excess of 1.3 equiv to correct for losses during addition. Each polymerization reaction was performed in duplo under exactly the same conditions to ensure a good reproducibility (see Experimental Section). Reaction time was 1 h unless stated otherwise. The resulting mixtures are precipitated in a nonsolvent (for the polymer), and both the polymer fraction and the low molecular fraction, from now on called residual fraction, were collected and analyzed. The molecular weight distribution, determined with size exclusion chromatography (SEC), was always monomodal unless stated otherwise. Because of weight loss during isolation of the products, the sum of polymer fraction and residual fraction is not equal to 100%. The residual fraction was always a mixture of maximum two products, unless stated otherwise. The ratio of these products, **1**:**9**, is determined with ^{1}H NMR. The chemical shifts of the different solvent-substituted products **9** were based on assignments of purified products. Chemical shifts of **9** (solvent = $N(CH_3)CHO$, R = *n*-Bu) are published elsewhere;[13] shifts of **9** (solvent = *s*-BuO, R = *n*-Oct) are presented in this paper.

Formation of the Actual Monomer, *p*-Xylylene 8. Polymerization of sulfinyl monomers such as **1** proceeds via the *p*-xylylene intermediate **8**. UV−vis spectroscopy has proven to be the most convenient technique, by which the concentration of polymerizing *p*-xylylenes in the Wessling process[14] can be monitored. Applying this technique for monitoring the appearance and depletion of *p*-xylylene intermediate **8** results in a plot as depicted in Figure 1. Because of the strong absorption of *p*-xylylenes in UV, the premonomer concentration used in these experiments (1.3 mM) is not similar to the concentration of a typical polymerization experiment (100 mM). Moreover, the base-to-premonomer ratio was changed to a large excess of base to ensure maximal equilibrium production of premonomer anion **7** to *p*-xylylene **8**. Under these conditions, production of *p*-xylylene **8** is strongly favored, while polymerization is disfavored. Hence, conditions are optimized to observe *p*-xylylene derivative **8**.

The position of the absorption maximum of **8g** (313 nm) is in good accordance with the known UV−vis spectra of *p*-xylylene[15] and the corresponding Wessling *p*-xylylene derivative.[14] Control comparison studies on nonpolymerizable sulfinyl monomers established that the absorptions are not due to anion **7g** formed from simple deprotonation. The absorption increases immediately after addition of base to premonomer **1g**, reaches a maximum intensity, and decreases to intensity of the blank, thus showing classical behavior for a reactive intermediate that is first generated and then depleted in a reaction.

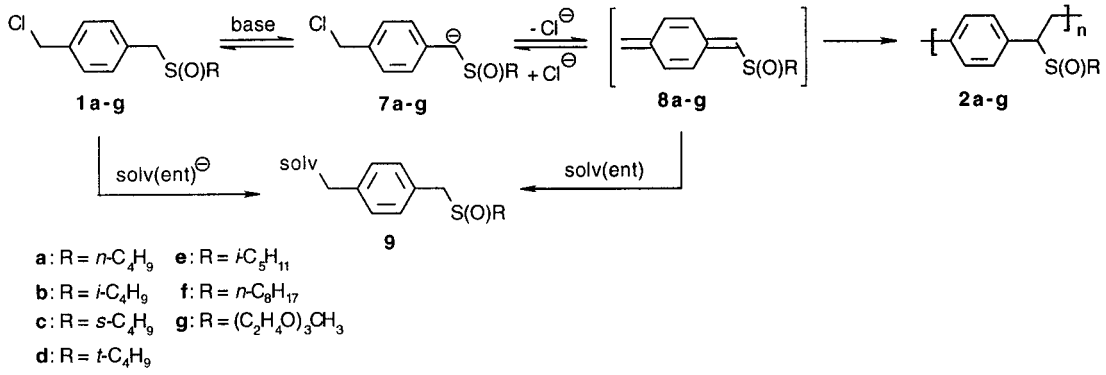
The first step in formation of **8** is proton abstraction of premonomer **1** by NaO*t*-Bu. In protic solvents, hydrogen bond donors (HBD solvents) like *N*-methylformamide (MMF), and alcohols there will be a base leveling effect as the actual base will be the solvent anion. In dipolar aprotic solvents, or better dipolar non-HBD solvents such as dimethyl sulfoxide (DMSO), the basicity as well as the nucleophilicity of the weakly solvated *t*-BuO anion is enhanced.

The second step, 1,6-elimination, is accounted for by expulsion of the chlorine leaving group. In this way the actual monomer, *p*-xylylene derivative **8**, is generated. This equilibrium can shift as a result of solvent effects. In non-HBD solvents both the premonomer anion **7** and the chloride anion will be weakly solvated, in comparison with HBD solvents. The chlorine anion is a much better nucleophile[16,17] in non-HBD solvents, and therefore a shift of the equilibrium toward the premonomer anion **7** cannot be excluded. Furthermore, **7** and **8** will be solvated to a different extent, according to the solvating power of the solvent used. This will have an effect on the total energy difference (ΔG) and the activation energy ($\Delta G^{\neq}$) between **7** and **8** and thus formation of **8**.

Polymerization of *p*-Xylylene 8. Once the *p*-xylylene intermediate is formed, it will polymerize spontaneously without external initiation. It has been shown previously[9] that in MMF initiation most probably occurs by dimerization of two *p*-xylylene intermediates with formation of a biradical. This biradical will propagate by a free radical mechanism. Because of the low pK_s (negative logarithm of autoprotolysis constant) of MMF (10.74),[18a] the actual base is the MMF anion. An important side reaction in these protic solvents is attack of the solvent anion at either the level of the premonomer or the *p*-xylylene intermediate leading to the solvent-substituted product **9**. This product cannot participate in the polymerization reaction anymore so there will be a decrease in polymer yield. Starting from premonomer **1a** (R = *n*-Bu), 24% precursor polymer **2a** was isolated together with 76% residual fraction as a mixture of **1a** and **9** (solvent = $N(CH_3)CHO$, R = *n*-Bu) in a 70:30 ratio.[19]

Polymerization in Non-HBD Solvents. One way to raise the polymer yield would be preventing solvent substitution to occur. By using a nonnucleophilic base (NaO*t*-Bu) in aprotic solvents, this could be realized. The results are collected in Table 1. An impor-

Scheme 3. Polymerization and Solvent Substitution of Sulfinyl Monomers



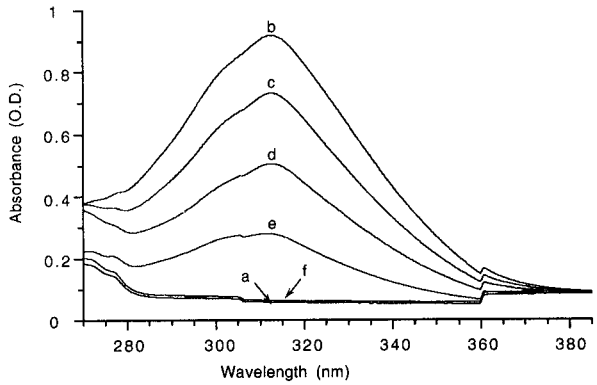


Figure 1. UV−vis spectra for **8g** (R = $(C_2H_4O)_3CH_3$). Spectra were obtained in *s*-BuOH at different time intervals under the conditions described in the Experimental Section. (a) Blank, (b) 0 min, (c) 0.5 min, (d) 1.0 min, (e) 1.5 min, (f) 2.0 min.

Table 1. Polymerization in Non-HBD Solvents

entry	monomer **1** (R)	solvent	polymer fraction (%)	residual fraction (%), (**1**: **9**)	$10^{-3}\,\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	*n*-octyl	CH_2Cl_2	76	12 (100:0)	350	2.4
2	*n*-octyl	THF	81	12 (100:0)	735	3.9[b]
3	*n*-octyl	DMSO	54	41 (100:0)	460	7.3[b]
4	*n*-octyl	DMSO[a]	45	52 (100:0)	186	14.1[b]

[a] Polymerization in the presence of 5 equiv of NaCl. [b] Bimodal molecular weight distribution.

tant feature of these solvents is the enhanced base strength. Sulfinyl precursor polymers are liable to base-induced elimination of sulfinyl groups on the backbone in these solvents. This will lead to conjugated segments in the precursor polymer and hence to different properties of the isolated polymer. To avoid this basic elimination, the experiments were performed with 1 equiv of base.

Indeed, no solvent substitution or substitution by the *t*-BuO anion occurs in these experiments. The residual fraction consists purely of premonomer. This results in a high polymer yield in the solvents CH_2Cl_2 and THF, but in DMSO the yield is only moderate. As stated before, the reactivity of the chloride anion, which is formed upon 1,6-elimination of **7**, is strongly enhanced in DMSO.[16,17] This could account for the relatively high amount of premonomer isolated, which is formed upon addition of a chloride anion to **8**. To verify this, polymerization was performed in the presence of 5 equiv of NaCl. In this way the polymer yield decreased from 54% to 45% in favor of premonomer **1** (Table 1, entry 4). Although not a large decrease, there seems to be an effect of addition of chloride anions.

Polymerization in HBD Solvents. Base-induced elimination of sulfinyl precursor polymers is an unwanted side reaction in non-HBD solvents. To prevent this, an equimolar amount of base has to be used. Another way of circumventing this problem is the use of HBD solvents. Because of a base leveling effect, the actual base will be much weaker as compared to (aprotic) non-HBD solvents. Alcohols are an important class of HBD solvents, which are also interesting from an environmental point of view. The results are collected in Table 2. Polymerization in MMF is also mentioned here as a reference experiment. In all cases basic elimination was not observed despite the use of 1.3 equiv of NaO*t*-Bu.

The results for both premonomers **1f** and **1g** are very much alike and will be discussed together. Polymer yields starting from **1g** are always slightly lower. The resulting precursor polymer **2g** is a very sticky material and thus more difficult to isolate.

The alcohols mentioned in Table 2 differ in physical properties such as for example polarity, pK_s, solubility of NaCl, and nucleophilicity of the solvent anion formed. Every property can have in itself an influence on the different steps in the polymerization process. Moreover, in going from one alcohol to another, all the properties mentioned will change rather independently. Since only the yield of polymer and yield and composition of the residual fraction can be determined accurately, the influence of the different alcohols on the polymerization reaction will be discussed in relation to these results.

As can be deduced from Table 2, the polymer yield varies between 0% in MeOH to almost 90% in branched alcohols such as *s*-BuOH, *t*-BuOH, and *s*-PeOH. For premonomer **1g** polymerization is even possible in water although only in a moderate yield. The residual fraction is always a mixture of premonomer **1** and solvent-substituted product **9**. These solvent-substituted products cannot participate in the polymerization process anymore. This was confirmed by an attempt to polymerize **9** (solvent = *s*-BuO, R = *n*-Oct) under standard polymerization conditions. In this way no precursor polymer could be isolated. Solvent substitution is therefore, as it is in MMF, a competitive process to polymerization, irrespective of the question whether this reaction occurs at the level of premonomer **1** or *p*-xylylene **8**. According to Bunnett,[20] nucleophilic reactivity depends on no fewer than 17 factors. Without taking into account all these factors, it is acceptable to state that in the series of linear alcohols, going from methanol to *n*-pentanol, the nucleophilicity of the corresponding anions will increase. The ratio of **1** to **9** indeed increases

Table 2. Polymerization in HBD Solvents

entry	monomer **1** (R)	solvent	polymer fraction (%)	residual fraction (%), (**1**:**9**)	$10^{-3}\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	*n*-octyl	MMF	28	69 (70:30)	780	3.0
2	*n*-octyl	MeOH	0	100 (92:8)		
3	*n*-octyl	EtOH	11	87 (20:80)	107	1.7
4	*n*-octyl	*n*-PrOH	30	62 (1:99)	118	1.7
5	*n*-octyl	*n*-BuOH	28	65 (4:96)	104	1.7
6	*n*-octyl	*n*-PeOH	42	56 (5:95)	100	1.7
7	*n*-octyl	*i*-PrOH	21	78 (11:89)	437	2.3
8	*n*-octyl	*s*-BuOH	88	4 (4:96)	238	2.0
9	*n*-octyl	*t*-BuOH	89	4 (19:81)	225	2.1
10	*n*-octyl	*s*-PeOH	89	5 (9:91)	296	2.4
11	$(C_2H_4O)_3CH_3$	H_2O	34	50 (100:0)	616	1.8
12	$(C_2H_4O)_3CH_3$	MeOH	0	99 (86:14)		
13	$(C_2H_4O)_3CH_3$	EtOH	9	78 (15:85)	375	1.9
14	$(C_2H_4O)_3CH_3$	*n*-PrOH	28	56 (2:98)	380	2.0
15	$(C_2H_4O)_3CH_3$	*n*-BuOH	27	53 (3:97)	388	1.8
16	$(C_2H_4O)_3CH_3$	*n*-PeOH	39	45 (5:95)	397	2.0
17	$(C_2H_4O)_3CH_3$	*i*-PrOH	18	62 (8:92)	455	2.4
18	$(C_2H_4O)_3CH_3$	*s*-BuOH	83	3 (8:92)	435	2.2
19	$(C_2H_4O)_3CH_3$	*t*-BuOH	82	3 (16:84)	405	2.3
20	$(C_2H_4O)_3CH_3$	*s*-PeOH	84	3 (5:95)	392	2.3

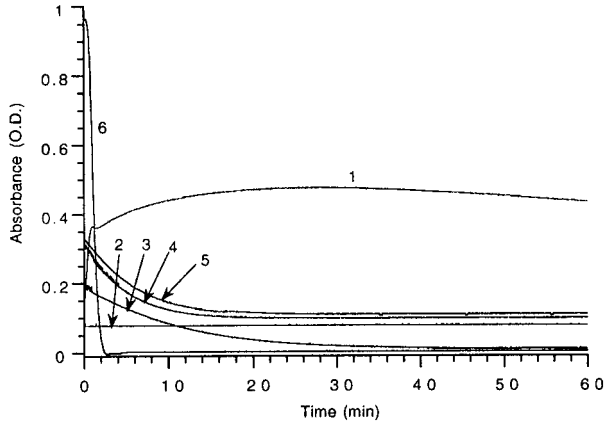


Figure 2. Change of absorption for **8g** (R = $(C_2H_4O)_3CH_3$) monitored in time. Spectra were obtained in (1) H_2O, (2) MeOH, (3) EtOH, (4) *n*-PrOH, (5) *n*-BuOH, and (6) *s*-BuOH.

in favor of **9** in this series. However, the polymer yield is also rising in the same direction, indicating that other factors are of equal or even more importance. On the other hand, the nucleophilicity of the anions of the branched alcohols will be lower, if compared to their linear analogues, because of steric requirements. Here the polymer yield is substantially higher, although the residual fraction still consists of almost pure solvent-substituted product.

For a high polymer yield an efficient conversion of premonomer **1** to actual monomer **8** is needed. Monitoring the formation of the actual monomer **8** by using UV−vis can give more information about this process. First, the wavelength position at maximum absorption of *p*-xylylene derivative **8g** was determined in different linear alcohols, *s*-butanol, and water. This position does not shift significantly by changing (the polarity of) the solvent (311−313 nm). In Figure 2 the change in absorption at the determined wavelength position was monitored.

Formation of the Actual Monomer in Alcohols. The absolute value of the absorption should be regarded with some care. The extinction coefficient of a compound can change in solvents of different polarity. Furthermore, the decrease of absorption, i.e., consumption of **8g**, will be caused by a combination of polymerization and solvent substitution. In these measurements a large excess of base is used, so consumption of **8g** will predominantly occur by solvent substitution. Taking into account these remarks, the trend in the maximum absorption of these curves still corresponds nicely with the trend in polymer yield. Going from methanol to *n*-butanol, there is both an increase in maximum absorption and an increase in polymer yield (Table 2). Methanol is a special case. In this solvent no *p*-xylylene derivative can be detected. This corresponds well with the fact that no polymer can be isolated. Since the pK_s of methanol (16.9)[18b] is higher than the pK_s of water (14.0),[18c] in which there is polymerization, it is likely that not deprotonation of premonomer **1** but conversion of the premonomer anion **7** to *p*-xylylene derivative **8** is the limiting step. This reaction is probably strongly disfavored in methanol. In the other linear alcohols the amount of **8** increases in going from ethanol to *n*-butanol, meaning that the overall process from **1** to **8** becomes more favorable. A number of properties such as pK_s and polarity change in this series of alcohols. The pK_s of these linear alcohols increases from 19.1 (ethanol)[18d] to 20.8 (*n*-pentanol).[18e] As a consequence, the base strength increases going from ethanol to *n*-pentanol. This will have an influence on the first step in the polymerization process, viz. proton abstraction, to afford premonomer anion **7**. The polarity of a solvent is not easily defined precisely and even more difficult to express quantitatively. Attempts to express it quantitatively involve mainly physical solvent properties such as dielectric constant, dipole moment, or refractive index. However, this approach is often inadequate since these theories regard solvents as a nonstructured continuum.[21] The most comprehensive solvent polarity scales are those derived from spectroscopic reference processes. The one based on E_T^N values is widely used, because of the broad range of solvents and binary solvent mixtures for which they were determined.[22,23] Water and tetramethylsilane (TMS) are used as extreme reference solvents with values of 1.000 and 0.000, respectively. For the linear alcohols these values are 0.762 (methanol), 0.654 (ethanol), 0.617 (*n*-propanol), 0.602 (*n*-butanol), and 0.568 (*n*-pentanol). This change in solvent polarity will have an effect on ΔG and $\Delta G^{\neq}$ between premonomer anion **7**, actual monomer **8**, and possible different intermediate ion pairs. In methanol these effects result in a strongly disfavored overall

Table 3. Polymerization in *n*-BuOH Quenched at Different Time Intervals.

entry	monomer **1** (R)	solvent	reaction time (min)	polymer fraction (%)	residual fraction (%), (**1**: **9**)	10^{-3} $\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	*n*-octyl	*n*-BuOH	1.5	8	86 (68:32)	133	1.6
2	*n*-octyl	*n*-BuOH	5	28	66 (49:51)	120	1.6
3	*n*-octyl	*n*-BuOH	10	28	66 (35:65)	110	1.7
4	*n*-octyl	*n*-BuOH	60	28	68 (4:96)	104	1.7

conversion of **7** to **8**. However, more experimental data are needed to elucidate this process completely.

In the branched *s*-butanol the maximum absorption (curve 6, Figure 2) is substantially higher if compared with the other solvents used. Apparently, conversion of premonomer to actual monomer in *s*-butanol is a very efficient process, resulting in a high polymer yield. If *s*-butanol is compared with *n*-butanol, the pK_s is higher and the E_T^N value is lower. Obviously the prerequisites for efficient formation of **8** are met in *s*-butanol.

Formation of the Actual Monomer in Water. Curve 1 (Figure 2) represents formation of **8g** in water. Here the maximum absorption is not reached at the beginning of the experiment, but only after 25 min. Thereafter, the concentration of **8g** remains more or less constant. Apparently **8g** is not as quickly consumed as in alcohols, probably because of a lower nucleophilicity of hydroxide anions in comparison to alcoholate anions.

Polymerization in Linear Alcohols. Solvent substitution in HBD solvents is a competitive process for polymerization and will lead to a decrease in polymer yield. To verify whether substitution occurs at the level of premonomer **1** or *p*-xylylene derivative **8**, two experiments were performed. α,α′-Dichloroxylene was used as a model compound for premonomer **1** to find out whether the benzylic chlorine is prone to substitution by an alcoholate anion. The reactivity of the benzylic chlorine of α,α′-dichloroxylene and that of **1** will be approximately the same, although some influence of the sulfinyl group in the para position cannot be excluded. The chemical shifts (both ^{1}H and ^{13}C) of the benzylic methylene of α,α′-dichloroxylene and that of **1** are almost identical, indicating that the electron densities at the benzylic carbon and proton are similar. First, it was established by UV−vis that, in both linear and branched alcohols at ambient temperature, α,α′-dichloroxylene does not give rise to the corresponding *p*-xylylene derivative. Second, upon reacting α,α′-dichloroxylene under standard polymerization conditions in *n*-BuOH, only 3% of monosubstituted product was isolated, while no disubstituted product could be detected. Obviously such a benzylic chlorine is not very reactive toward *n*-BuO anions. If a comparable reactivity of the benzylic chlorine of premonomer **1** is assumed, this would mean that solvent substitution occurs mainly at the level of *p*-xylylene derivative **8**. Consequently, the amount of polymer together with the amount of solvent-substituted product is a measure of the overall production of *p*-xylylene derivative.

Except for methanol and ethanol, the overall production of *p*-xylylene derivative is almost quantitative after 1 h according to the sum of polymer yield and yield of **9** (entries 2−6, entries 12−16, Table 2). If subsequent polymerization experiments in *n*-butanol are quenched at different time intervals, an interesting phenomenon is observed. The results are collected in Table 3.

After 1.5 min a minor amount of precursor polymer is formed together with a residual fraction consisting of 32% of solvent substituted product **9**. Somewhere between 1.5 and 5 min after addition of the base no additional precursor polymer is formed. However, the amount of solvent-substituted product **9** still increases with increasing reaction time in disfavor of premonomer **1**, resulting in a residual fraction that consists of almost pure **9** after 1 h reaction time.

At this moment, no rate constants for initiation, propagation, termination, or chain transfer are available for this polymerization process. Recently Cho[24] found a k_p in the range $(0.105-1.32) \times 10^8$ M^{-1} s^{-1} for similar *p*-xylylene derivatives. This large value can readily be understood if the high reactivity of these derivatives is considered.[25] As stated before, initiation most probably occurs by dimerization of two *p*-xylylene derivatives with formation of a biradical, which can propagate by a radical chain mechanism. Therefore, the *p*-xylylene concentration will be raised to a square in the initiation rate equation. Initiation and subsequent propagation will only start at a certain critical *p*-xylylene concentration. On the contrary, in the presence of solvent anions, solvent substitution can still occur at *p*-xylylene concentrations which are below this critical concentration. This could explain the still increasing amount of **9** in the residual fraction at reaction times exceeding 5 min, while the amount of polymer remains constant. After 5 min the steady-state *p*-xylylene concentration is not sufficient anymore to initiate polymerization but still allows attack of solvent anions to give **9**.

Polymerization in *s*-BuOH. To gain more information about the efficient polymerization in *s*-butanol, this solvent was investigated in more detail. The existence of the biradical initiator was confirmed by an experiment in which the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was added in a polymerization reaction (entry 2, Table 4). TEMPO inhibits polymerization almost completely. A significant part (40%) of the residual fraction of the TEMPO experiment consists of a dialdehyde which was attributed[9] to result from the trapped biradical mentioned before. Results of experiments in which the chain transfer agent tetrabromomethane (CBr_4) is added in *s*-butanol (entry 3, Table 4) showed that the molecular weight decreased by a factor of 4, while the polymer yield was comparable with that of a standard polymerization.

In a normal polymerization initiation will only start at a certain critical concentration of **8**. In *s*-butanol this concentration will be reached very quickly because of the fast buildup of *p*-xylylene derivative as was demonstrated by the UV−vis experiments. Considering the high reactivity of **8**, polymerization will be overall a very fast process. This is confirmed by an experiment in which the reaction was quenched after 10 s (entry 4, Table 4). In this experiment 64% of high molecular weight precursor polymer could be isolated against 88% if a reaction time of 1 h is maintained.

In *s*-butanol two experiments were performed to verify whether solvent substitution also occurs at the level of *p*-xylylene derivative **8**. As described before for *n*-butanol, α,α′-dichloroxylene was used as a model compound for premonomer **1**. In *s*-butanol no solvent substitution occurred upon reacting α,α′-dichloroxylene

Table 4. Polymerization in *s*-BuOH under Different Conditions

entry	monomer **1** (R)	solvent	polymer fraction (%)	residual fraction (%), (**1**: **9**)	$10^{-3}\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	*n*-octyl	*s*-BuOH[a]	88	4 (4:96)	249	3.0
2	*n*-octyl	*s*-BuOH[b]	2	96 (*b*)	93	2.0
3	*n*-octyl	*s*-BuOH[c]	84	12 (4:96)	58	2.1
4	*n*-octyl	*s*-BuOH[d]	64	32 (77:23)	270	2.5
5	*n*-octyl	*s*-BuOH[e]	22	72 (0:100)	230	2.1
6	*n*-octyl	*s*-BuOH[f]	42	54 (94:6)	236	2.7
7	*n*-octyl	*s*-BuOH[g]	80	16 (0:100)	244	3.2
8	*n*-octyl	*s*-BuOH[h]	87	10 (100:0)	203	2.8
9	*n*-octyl	*s*-BuOH[i]	30	65 (100:0)	47	1.8
10	*n*-octyl	*s*-BuOH[j]	41	55 (100:0)	37	2.3

[a] Standard polymerization. [b] Polymerization in the presence of 0.5 equiv of TEMPO, residual fraction consists of **1**:**9**:dialdehyde in a 3:57:40 ratio. [c] Polymerization in the presence of 0.5 equiv of CBr_4. [d] Polymerization quenched after 10 s. [e] Polymerization in the presence of 5 mol % 18-crown-6. [f] Polymerization in the presence of 0.5 equiv of NaO*t*-Bu. [g] Polymerization in the presence of 2 equiv of NaO*t*-Bu. [h] Polymerization with NaOH. [i] Polymerization in the presence of 5% (v/v) H_2O, 1 h reaction time. [j] Polymerization in the presence of 5% (v/v) H_2O, 3 h reaction time.

Table 5. Polymerization of Different Sulfinyl Monomers in *s*-BuOH

entry	monomer **1** (R)	solvent	polymer fraction (%)	residual fraction (%), (**1**: **9**)	$10^{-3}\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	*n*-butyl	*s*-BuOH	87	6 (6:94)	540	2.5
2	*i*-butyl	*s*-BuOH	87	7 (5:95)	280	2.2
3	*s*-butyl	*s*-BuOH	78	14 (6:94)	260	2.2
4	*t*-butyl	*s*-BuOH	77	16 (4:96)	42	1.9
5	*i*-pentyl	*s*-BuOH	88	6 (4:96)	500	2.3
6	*n*-octyl	*s*-BuOH	88	4 (4:96)	238	2.0
7	$(C_2H_4O)_3CH_3$	*s*-BuOH	83	8 (8:92)	435	2.2

under standard polymerization conditions. Even if the nucleophilicity of the *s*-BuO anions is enhanced by adding 5 mol % of 18-crown-6, only 2% of monosubstituted product is obtained, while no disubstituted product could be detected. From these experiments it became clear that also in *s*-butanol solvent substitution occurs mainly at the level of *p*-xylylene derivative **8**. If so, the large decrease in polymer yield and the large increase in solvent-substituted product upon addition of 5 mol % of 18-crown-6 to a polymerization (entry 5, Table 4) can only be explained by a strongly favored addition of *s*-BuO anions to **8**. This would mean that by enhancing the nucleophilic reactivity of the *s*-BuO anion the difference in rate constants for solvent substitution and propagation increases in favor of the first. If the concentration of *s*-BuO anions is increased by using 2 equiv of base (entry 7, Table 4) instead of 1.3, this also leads to a decrease in polymer yield in favor of solvent substituted product. For this particular system 1 equiv of base would therefore be the best choice.

In a standard polymerization NaO*t*-Bu is used as the base. Changing from NaO*t*-Bu to NaOH does not have an effect on the polymer yield (entry 8, Table 4), but the residual fraction consists of 100% premonomer, indicating that no substitution whatsoever had occurred. When NaOH is used as the base, the hydroxide anion will be the actual base instead of the *s*-BuO anion. According to the polymer yield, formation of the actual monomer is not influenced by this change. Because of the apparent low nucleophilic reactivity of the hydroxide anion in this process, no side reaction will occur and polymerization will be favored. This would also implicate that by using NaOH 100% conversion to polymer should be possible.

When comparing entries 9 and 10 (Table 4), in which 5% v/v water (corresponds to a ratio of 96.5 mol % water and 3.5 mol % premonomer **1**) is added to the reaction mixture, a couple of results draw attention. In both cases only premonomer is present in the residual fraction. This is in agreement with the experiment in which NaOH was used as the base. By addition of water, hydroxide anions are generated in situ which do not induce a substitution reaction. Furthermore, by using the usual 1 h of reaction time, the polymer yield is reduced to only 30%. Extension of the reaction time to 3 h leads to an increase of the polymer yield to 41%. It is clear that polymerization is retarded by addition of water. Probably, the change in solvent polarity induced by addition of water affects the solvation of **7** and *p*-xylylene derivative **8**, leading to a relatively slow formation of **8**. Since there is no side reaction by substitution possible, further elongation of reaction time could still induce an increase in polymer yield. The molecular weight decreases by a factor of 6, when compared to a standard polymerization. Assuming a comparable critical *p*-xylylene concentration at which initiation starts, this can be explained by the fact that because of the slow formation of **8**, the amount of **8** available for propagation will be relatively small, resulting in a decrease in molecular weight.

By changing the R group of the sulfinyl monomers, the polymer yield and yield of residual fraction are also somewhat affected. The results are collected in Table 5. For monomers with linear R groups (entries 1 and 6, Table 5) polymer yields as well as yield of residual fractions are comparable. Incorporation of branches in the R group has an effect when the methyl group(s) are in the α-position of the sulfinyl group. These monomers show a decrease in polymer yield in favor of solvent-substituted product (entries 3 and 4, Table 5). It is obvious that if there is an effect of these bulky R-groups, it will be mainly expressed during propagation. Therefore, it is probably a steric effect by which solvent substitution is somewhat favored compared to polymerization.

Conclusions

Polymerization of sulfinyl monomers proceeds via the *p*-xylylene derivative **8** as was demonstrated by UV−

vis measurements. For a high polymer yield an efficient conversion of premonomer **1** to the actual monomer, *p*-xylylene derivative **8**, is essential. This actual monomer can undergo two reactions, viz. polymerization and/or solvent substitution. Solvent substitution probably occurs for the main part at the level of **8** as was shown by experiments with the model compound α,α′-dichloro-*p*-xylene. Once the solvent-substituted product **9** is formed, it cannot participate in the polymerization process anymore and will thus lower the polymer yield.

At a certain critical concentration of **8** initiation and subsequent polymerization will start. For the linear alcohol, *n*-butanol, it was shown that, somewhere between 1.5 and 5 min after addition of base, no additional polymer is formed. However, the amount of solvent-substituted product still increases. This would be indicative of a concentration of **8** that is below the critical concentration for initiation. In presence of solvent anions **8** can still undergo substitution. In the branched alcohols formation of **8** is a very fast process, and this critical concentration will be reached very quickly. This results in a high polymer yield (90%) and a residual fraction consisting of almost pure solvent-substituted product, which means that overall conversion of premonomer to actual monomer is approximately quantitative. Apparently the rate constant for polymerization in these alcohols exceeds the rate constant for substitution since a high polymer yield is found together with a minor amount of solvent-substituted product. Addition of water to the polymerization reaction retards the polymerization process considerably. Probably, the change in solvent polarity induced by addition of water affects the solvation of **7** and *p*-xylylene derivative **8**, leading to relatively slow formation of **8**. Since there is no side reaction by substitution possible, further elongation of reaction time could still induce an increase in polymer yield. The molecular weight decreases by a factor of 6 in comparison to a standard polymerization. Assuming a comparable critical *p*-xylylene concentration at which initiation starts, this can be explained by the fact that because of the slow formation of **8**, the amount of **8** available for propagation will be relatively small, resulting in a decrease in molecular weight.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. All reactions were performed under an inert atmosphere of nitrogen.

Monomers 1a−g. Synthesis of monomers **1a−g** will be described elsewhere.[12]

Precursor Polymers 2a−g. General Procedure. A solution of monomer (2 mmol) in solvent (14 mL) and a solution of sodium *tert*-butoxide (0.25 g, 2.6 mmol) in solvent (6 mL) were degassed for 1 h at 30 °C by passing through a continuous stream of nitrogen. The base solution was added in one portion. After 1 h the reaction mixture was poured in a well-stirred amount (200 mL) of ice water. The mixture was neutralized with aqueous hydrogen chloride (1 M) and extracted with $CHCl_3$ (3 × 100 mL). The combined organic layers were concentrated in vacuo. The crude product was dissolved in $CHCl_3$ (12.5 g) and precipitated in a mixture of *n*-hexane: diethyl ether 1:1, w/w (125 g). The polymer was collected and dried in vacuo. The residual fraction was concentrated in vacuo.

Poly[*p*-phenylene(1-*n*-butylsulfinyl)ethylene] (2a). This compound was synthesized according to the general procedure starting from **1a** (0.49 g) to give **2a** as a white solid (0.34 g, 82%): $\bar{M}_w$ = 540 000, $\bar{M}_w/\bar{M}_n$ = 2.5. T_g = 68 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.6−0.9 (3H, br), 1.1−1.4 (2H, br), 1.4−1.7 (2H, br), 1.8−2.1 + 2.1−2.5 (2H, br), 2.9−3.3 (1H), 3.3−3.9 (2H, br), 6.7−7.5 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 22.4 + 22.6, 24.9 + 25.5, 36.6 + 36.9, 49.6 + 50.2, 65.8 + 70.6, 129.0, 129.3, 129.6, 130.0, 130.5, 131.9, 132.2, 132.9, 133.1, 138.8 ppm. IR (KBr): ν 2958, 2929, 2871, 1031 cm^{-1}. Anal. Calcd for $(C_{12}H_{16}OS)_n$: C, 69.19; H, 7.74; S, 15.39. Found: C, 66.86; H, 7.57; S, 14.33. The large deviation can be attributed to water present on the precursor polymer. Water determination by Karl Fischer titration and ^{1}H NMR gave a water content of 42 mol %. The analytically calculated values for $(C_{12}H_{16}OS)_n$ are therefore: C, 66.76; H, 7.86; S, 14.33.

Poly[*p*-phenylene(1-*iso*-butylsulfinyl)ethylene] (2b). This compound was synthesized according to the general procedure starting from **1b** (0.49 g) to give **2b** as a white solid (0.34 g, 82%): $\bar{M}_w$ = 280 000, $\bar{M}_w/\bar{M}_n$ = 2.2. T_g = 98 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.82 + 0.89 (6H, br), 1.7−2.2 + 2.25−2.45 (3H, br), 2.75−3.35 (1H), 3.35−3.8 (2H, br), 6.7−7.2 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.3 + 21.7, 22.8, 23.6 + 23.8, 30.6 + 31.3, 35.7 + 36.3, 58.2 + 59.8, 65.5 + 70.6, 128.4, 128.6, 128.9, 129.4, 129.9, 131.2, 131.5, 132.2, 138.1 ppm. IR (KBr): ν 2958, 2928, 2870, 1035 cm^{-1}.

Poly[*p*-phenylene(1-*sec*-butylsulfinyl)ethylene] (2c). This compound was synthesized according to the general procedure starting from **1c** (0.49 g) to give **2c** as a white solid (0.32 g, 78%): $\bar{M}_w$ = 260 000, $\bar{M}_w/\bar{M}_n$ = 2.2. T_g = 97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.60−1.25 (6H, br), 1.25−1.5 (1H, br), 1.5−1.75 (1H, br), 1.75−2.3 (1H, br), 2.75−3.35 (1H), 3.35−3.9 (2H, br), 6.6−7.2 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.3, 9.4, 10.1, 10.5, 10.8, 10.9, 11.4, 11.9, 12.1, 14.1, 20.6, 25.4, 31.3, 36.7, 47.2 + 52.2, 65.8 + 66.4, 128.2, 128.4, 128.7, 129.3, 129.9, 132.2, 132.6, 138.1 ppm. IR (KBr): ν 2965, 2931, 2873, 1035 cm^{-1}.

Poly[*p*-phenylene(1-*tert*-butylsulfinyl)ethylene] (2d). This compound was synthesized according to the general procedure starting from **1d** (0.49 g) to give **2d** as a white solid (0.32 g, 77%): $\bar{M}_w$ = 42 000, $\bar{M}_w/\bar{M}_n$ = 1.9. T_g = 109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.7−1.1 (9H, br), 2.6−3.25 (1H), 3.25−3.85 (2H, br), 6.5−7.1 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.7, 38.1 + 39.8, 54.8 + 55.6, 61.0 + 64.4 + 64.8, 128.7, 128.9, 129.2, 129.7, 133.7 + 133.8, 137.5 ppm. IR (KBr): ν 2960, 2926, 2902, 2866, 1033 cm^{-1}.

Poly[*p*-phenylene(1-*iso*-pentylsulfinyl)ethylene] (2e). This compound was synthesized according to the general procedure starting from **1e** (0.52 g) to give **2e** as a white solid (0.37 g, 83%): $\bar{M}_w$ = 500 000, $\bar{M}_w/\bar{M}_n$ = 2.3. T_g = 88 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.70 + 0.79 (6H, br), 1.2−1.7 (3H, br), 1.9−2.1 + 2.1−2.4 (2H, br), 2.75−3.35 (1H), 3.35−3.8 (2H, br), 6.7−7.2 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.7 + 22.1 + 22.4, 27.2 + 27.6, 30.6 + 31.3, 35.9 + 36.3, 47.2 + 47.7, 65.0 + 69.8, 128.3, 128.6, 128.9, 129.4, 129.9, 131.2, 131.5, 132.2, 138.2 ppm. IR (KBr): ν 2956, 2926, 2868, 1037 cm^{-1}.

Poly[*p*-phenylene(1-*n*-octylsulfinyl)ethylene] (2f). This compound was synthesized according to the general procedure starting from **1f** (0.60 g) to give **2f** as a transparent solid (0.47 g, 88%): $\bar{M}_w$ = 238 000, $\bar{M}_w/\bar{M}_n$ = 2.0. T_g = 49 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.75−0.9 (3H, br), 1.05−1.4 (10H, br), 1.4−1.75 (2H, br), 1.8−2.1 + 2.1−2.4 (2H, br), 2.75−3.35 (1H), 3.35−3.85 (2H, br), 6.7−7.3 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 22.3 + 22.5, 22.9, 22.9, 28.6, 28.9, 29.0, 31.6, 35.9 + 36.3, 49.2 + 49.8, 65.1 + 69.9, 128.0, 128.5, 128.9, 129.3, 129.8, 131.3, 131.6, 132.3, 132.5, 133.1, 138.1 ppm. IR (KBr): ν 2955, 2926, 2855, 1041 cm^{-1}.

Poly[*p*-phenylene(1-{2-[2-(2-methoxyethoxy)ethoxy]-ethyl}sulfinyl)ethylene] (2g). This compound was synthesized according to the general procedure starting from **1g** (0.67 g) to give **2g** as a light yellow solid (0.50 g, 83%): $\bar{M}_w$ = 435 000, $\bar{M}_w/\bar{M}_n$ = 2.2. T_g = 7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.95−2.1 + 2.3−2.65 (2H, br), 2.75−3.25 (1H), 3.25−3.35 (3H, br), 3.42−3.52 (2H, br), 3.52−3.7 + 3.7−3.9 (10H, br), 6.75−7.3 (4H, br) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.0, 49.5, 58.9, 63.3 + 64.1, 65.4 + 69.7, 70.3, 71.7, 128.7, 129.2, 129.8, 131.6, 132.0, 138.2 ppm. IR (KBr): ν 2955, 2926, 2855, 1104, 1041 cm^{-1}.

1-((Methylpropoxy)methyl)-4-[(*n*-octylsulfinyl)methyl]-benzene 9 (S = *s*-BuO). The low molecular weight fraction

of polymerization of **1f** in *s*-BuOH was purified by column chromatography (SiO_2, hexane/ethyl acetate 3:2) to give **9** as a light yellow waxy material. $R_f = 0.13$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.85 (t, $J = 6.8$ Hz, 3H), 0.91 (t, $J = 7.6$ Hz, 3H), 1.17 (d, $J = 6.0$ Hz, 3H), 1.23 (m, 8H), 1.36 (m, 2H), 1.47 + 1.60 (m, 2H), 1.70 (m, 2H), 2.52 (t, $J = 7.8$ Hz, 2H), 3.43 (m, 1H), 3.90 + 4.00 (dd, $J_{AB} = 12.8$ Hz, 2H), 4.44 + 4.53 (dd, $J_{AB} = 11.6$ Hz, 2H), 7.23 + 7.34 (dd, $J_{AB} = 8.0$ Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.7, 13.9, 19.0, 22.3, 22.4, 28.6, 28.8, 29.0, 31.6, 50.6, 57.9, 69.6, 127.9, 128.7, 129.8, 139.3. IR (KBr): υ 2959, 2918, 2847, 1100, 1026 cm^{-1}. MS (EI, *m*/*z*, rel int (%)): 338 ([M]$^+$, not detected), 265 ([$C_{16}H_{25}OS$]$^+$, 2), 177 ([$C_{12}H_{17}O$]$^+$, 100), 121 ([C_8H_9O]$^+$, 87), 104 ([C_8H_8]$^+$, 30), 57 ([C_4H_9]$^+$, 13). Anal. Calcd for $C_{20}H_{34}O_2S$: C, 70.96; H, 10.12; S, 9.47. Found: C, 70.90; H, 10.18; S, 9.33.

Polymerization in THF, CH_2Cl_2, DMSO. To prevent basic elimination of sulfinyl groups, polymerization was carried out with 1 equiv of NaO*t*Bu. For polymerization in CH_2Cl_2 the monomer was dissolved in 20 mL, and NaO*t*Bu was introduced in its solid state.

UV−vis Spectroscopy. All solvents used in preparation of the solutions were thoroughly purged with nitrogen before use. A magnetic stirrer was incorporated in the sample holder of the UV−vis spectrometer to achieve efficient mixing of the reagents. Spectra were acquired from 200 to 400 nm at programmed time intervals, or the change in λ_{max} was monitored in time (1 h). Scan rate was ca. 2000 nm/min and the sampling interval 0.2 nm.

A stock solution of **1g** was made by dissolving 34.9 mg (104.2 μmol) in MeOH (5 mL, 3.96 g) to generate a 20.8 mM solution. The same concentration was used for all other solvents.

A stock solution of NaO*t*-Bu was made by dissolving 1250.0 mg (13.0 mmol) in MeOH (12.5 mL, 9.9 g) to generate a 1.04 M solution. The same concentration was used for all other solvents.

Monitoring Polymerization. Stock solution of **1g** (100 μL) was transferred by syringe to a quartz cuvette and diluted with MeOH (1.5 mL). A blank spectrum was recorded at 25 °C against a MeOH reference. Next, NaOtBu solution (100 μL) was injected in the cuvette to generate a 1.3 mM solution in **1g**, and spectra were obtained at different programmed time intervals or the change in absorption at λ_{max} was monitored in time.

Instrumentation. ^{1}H NMR spectra were obtained in $CDCl_3$ at 400 MHz on a Varian Inova spectrometer using a 5 mm probe. Chemical shifts (δ) in ppm were determined relative to the residual $CHCl_3$ absorption (7.24 ppm). The ^{13}C NMR experiments were recorded at 100 MHz on the same spectrometer using a 5 mm broad-band probe. Chemical shifts were defined relative to the ^{13}C resonance shift of $CHCl_3$ (77.0 ppm). Resonance assignments were achieved by the use of one- and two-dimensional NMR techniques such as ^{1}H, ^{13}C, APT, 2D HETCOR ($J = 140$ Hz), 2D FLOCK ($J = 23$ Hz), 2D INADEQUATE, and 2D COSY and will be desribed elsewhere.[26] Fourier transform infrared spectroscopy is performed on a Perkin-Elmer 1600 FT-IR (nominal resolution 2 cm^{-1}, summation of 16 scans). Molecular weights were determined relative to polystyrene standards by size exclusion chromatography on a Spectra series P100 (Spectra Physics) equipped with MIXED-B columns (10 μm, 2 × 30 cm, Polymer Labs) using a DMF solution of oxalic acid (1 mM) as the eluent at 70 °C or THF at 40 °C with a flow rate of 1 mL min^{-1} and a RI detector (Shodex). Glass transition temperatures were measured by modulated temperature differential scanning calorimetry on a TA Instruments 2000. Heating rates were 3 °C/min, amplitude was 0.35 °C, period was 1 min, and T_g was taken as the midpoint of the inflection tangent.

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References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.
(3) Wessling, R. A.; Zimmerman, R. G. U.S. Patent 3401152, 1968.
(4) Wessling, R. A. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 55.
(5) Lenz, R. W.; Han, C.-C.; Stenger-Smith, J.; Karasz, F. E. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 3241.
(6) Burn, P. L.; Bradley, D. D. C.; Friend, R. H.; Halliday, D. A.; Holmes, A. B.; Jackson, R. W.; Kraft, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3225.
(7) Garay, R. O.; Baier, U.; Bubeck, C.; Müllen, K. *Adv. Mater.* **1993**, *5*, 561.
(8) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376.
(9) Issaris, A.; Vanderzande, D.; Gelan, J. *Polymer* **1997**, *38*, 2571.
(10) Van Der Borght, M.; Vanderzande, D.; Gelan, J. *Polymer* **1998**, *39*, 4171.
(11) Vanderzande, D. J.; Issaris, A. C.; Van Der Borght, M. J.; van Breemen, A. J.; de Kok, M. M.; Gelan, J. M. *Macromol. Symp.* **1997**, *125*, 189.
(12) van Breemen, A. J. J. M.; Vanderzande, D. J. M.; Adriaensens, P. J.; Gelan, J. M. J. V. *J. Org. Chem.* **1999**, *64*, 3106.
(13) Issaris, A.; Vanderzande, D.; Adriaensens, P.; Gelan, J. *Macromolecules* **1998**, *31*, 4426.
(14) Denton, F. R. III; Lahti, P. M.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2223.
(15) Pearson, J. M.; Six, H. A.; Williams, D. J.; Levy, M. *J. Am. Chem. Soc.* **1971**, *93*, 5034.
(16) Parker, A. J. *Q. Rev.* **1962**, *16*, 163.
(17) Parker, A. J. *Pure Appl. Chem.* **1981**, *53*, 1437.
(18) (a) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents: Physical Properties and Methods for Purification*, 4th ed.; Wiley-Interscience: New York, 1986; p 655, (b) p 191, (c) p 74, (d) p 193, (e) p 206.
(19) Issaris, A. C. J. Ph.D. dissertation, Limburgs Universitair Centrum Diepenbeek, 1997.
(20) Bunnett, J. F. Nucleophilic Reactivity. *Annu. Rev. Phys. Chem.* **1963**, *14*, 271.
(21) Reichardt, C. In *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH Verlagsgesellschaft: Weinheim, Germany, 1988.
(22) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1. Dimroth, K.; Reichardt, C. *Liebigs Ann. Chem.* **1969**, *727*, 93. Reichardt, C. *Liebigs Ann. Chem.* **1971**, *752*, 64. Dimroth, K.; Reichardt, C. *Fortschr. Chem. Forsch.* **1968**, *11*, 1.
(23) Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1983**, 721.
(24) Cho, B. R.; Kim, Y. K.; Han, M. S. *Macromolecules* **1998**, *31*, 2098.
(25) (a) Errede, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1957**, *79*, 4952. (b) Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 436. (c) Errede, L. A.; Pearson, W. A. *J. Am. Chem. Soc.* **1961**, *83*, 954.
(26) van Breemen, A. J. J. M.; de Kok, M. M.; Adriaensens, P. J.; Vanderzande, D. J. M.; Gelan, J. M. J. V. Manuscript in preparation.

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