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Synthesis of aromatic polyethers by Scholl reaction

III. On the polymerizability of 4,4'-di(1-naphthoxy)diphenyl sulfone and 1,5-di(1-naphthoxy)pentane*

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SUMMARY

The polymerizability of 4,4'-di(1-naphthoxy)diphenyl sulfone (**1**) and 1,5-di(1-naphthoxy)pentane (**2**) has been investigated under the oxidative polymerization (Scholl reaction) conditions. The polymerization of monomer **1** has consistently produced polymers of higher overall yields and number average molecular weights. The higher polymerizability of monomer **1** was discussed based on a radical-cation polymerization mechanism. Monomer **1** is less reactive than monomer **2**, while the radical-cation growing species derived from monomer **1** is more reactive than that derived from monomer **2**. In these polymerizations, the overall polymerizability is determined by the difference in the reactivity of monomers and of their corresponding radical-cation growing species. A discussion on the selectivity as indicated by the polymer gel content also provides additional evidence for the difference in the reactivities between the growing species.

INTRODUCTION

Recently we have developed a novel method for the synthesis of aromatic polyether sulfones and polyether ketones.[1,2] It consists of the dehydrogenative crosscoupling polymerization of aromatic ether sulfone and ether ketone monomers through an oxidative polymerization reaction (Scholl reaction).[3,4] The monomers investigated so far include, 4,4'-di(1-naphthoxy)diphenyl sulfone,[1] 4,4'-di(1-naphthoxy)benzophenone,[1] 4,4'-di(1-phenoxy)diphenyl sulfone,[2] 4,4'-di(1-phenylthio)diphenyl sulfone,[2] and 4,4'-di(1-phenoxy)diphenyl sulfone substituted with a variety of electron-donating substituents.[2] Monomers of different structures have revealed distinct reactivity during this polymerization. A radical-cation mechanism[1,2] was proposed for this polymerization. The control of this polymerization reaction requires information about the reactivity of monomers and growing species of various structure, and on the overall polymerizability of the monomers. This information is not available since most of the polymerizations reported so far were performed under different experimental conditions.[1,5]

This paper describes a series of experiments which will provide information on the polymerizability of 4,4'-di(1-naphthoxy)diphenyl sulfone and 1,5-di(1-naphthoxy)pentane.

EXPERIMENTAL

Materials

4,4'-Di(1-naphthoxy)diphenyl sulfone[1] (**1**) and 1,5-di(1-naphthoxy)pentane[5] (**2**) were synthesized as described. Anhydrous $FeCl_3$ (Aldrich) was used as received. Nitrobenzene (Fischer) was distilled from CaH_2.

Techniques

Relative molecular weights were determined by gel permeation chromatography (GPC). GPC measurements were obtained on a Perkin-Elmer series 10LC instrument equipped with a LC-100 column oven, LC 600 autosampler, and a Nelson Analytical data station. The measurements were made using a UV detector set at 254 nm, chloroform as solvent (1mL/min, 40°C), a set of PL-Gel columns of 500 and 10000 Å, and a calibration

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*Part II: V. Percec, J. H. Wang, Y. Oishi: J. Polym. Sci. Polym. Chem. Ed., submitted

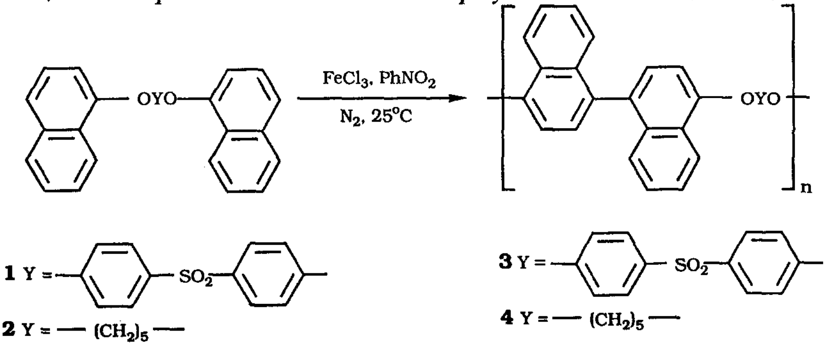
**To whom offprint requests should be sent plot constructed with polystyrene standards (Supelco). 200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as internal standard.

Polymerization of 4,4'-Di(1-naphthoxy)diphenyl Sulfone and of 1,5-Di(1-Naphthoxy)pentane

The polymerization procedure used in all experiments was identical to that previously described.[1,2] Detailed experimental conditions are listed in Table I. The total polymer yield is based on the overall weight of the polymer separated by precitation into methanol, followed by washing with boiling methanol. The polymer was then dissolved in boiling $CHCl_3$, and the insoluble fraction was separated by filtration to yield the gel fraction. The chloroform solution was then precipitated into methanol, and the reprecipitated polymer yielded the soluble polymer fraction.

RESULTS AND DISCUSSION

The oxidative polymerizations of 4,4'-di(1-naphthoxy)diphenyl sulfone (**1**) and 1,5-di(1-naphthoxy)diphenyl sulfone (**2**) are outlined in Scheme I. Both polymerizations were performed under a N_2 atmosphere in dry nitrobenzene using $FeCl_3$ as oxidant. The polymerization of **1** and **2** leads to polymers **3** and **4** respectively. In this study, the molar concentrations of both monomers and anhydrous $FeCl_3$ were maintained constant. The polymerization experiments were performed at four different reaction times, i.e. 0.5 h, 1.0 h, 2.0 h, and 4.0 h respectively. The $[FeCl_3]/[Monomer]$ molar ratio was maintained equal to 4/1. The experimental conditions and the polymerization results are listed in Table I.



(eq 1)

Scheme I. The oxidative polymerization of 4,4'-di(1-naphthoxy)diphenyl sulfone (**1**) and 1,5-di(1-naphthoxy)pentane (**2**).

In all polymerization experiments, an insoluble polymer fraction was obtained. The total polymer yield, which includes the gel and the soluble fractions, is plotted in Figure 1

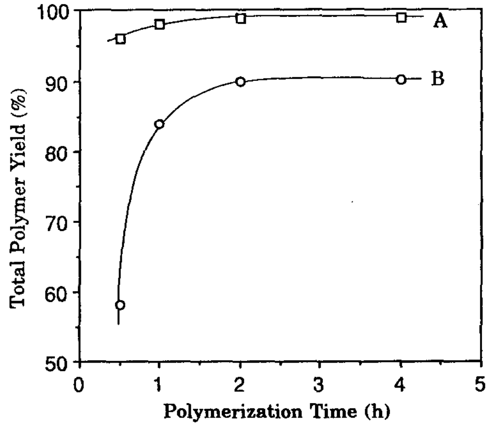


Figure 1. The dependence of total polymer yield on the polymerization time: A) polymerization of 4,4'di-(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-di(1-naphthoxy)pentane.

Table I. Influence of Polymerization time on the Polymerization of 4,4'-Di(1-Naphthoxy)Diphenyl Sulfone (**1**) and 1,5-Di(1-Naphthoxy)Pentane (**2**). Polymerization Temperature, 25°C.

Exp. No.	Monomer Solution		$FeCl_3$ Solution		Reaction Time (h)	Total Polymer Yield (%)	Gel Yield (%)	Soluble Polymer Fraction		
	Monomer/mmol	$PhNO_2$ (mL)	$FeCl_3$ (mmol)	$PhNO_2$ (mL)				Yield (%)	$\overline{M}_n$ (g/mol)	$\overline{M}_w/\overline{M}_n$
1	**1**/1.0	1.0	4.0	2.5	0.5	96.0	5.8	90.2	5800	4.98
2	**1**/1.0	1.0	4.0	2.5	1.0	98.1	6.2	91.9	8800	4.36
3	**1**/1.0	1.0	4.0	2.5	2.0	98.7	18.5	80.2	71100	2.08
4	**1**/1.0	1.0	4.0	2.5	4.0	98.9	19.0	79.9	40700	2.61
5	**2**/1.0	1.0	4.0	2.5	0.5	58.2	3.2	55.0	14900	4.45
6	**2**/1.0	1.0	4.0	2.5	1.0	84.1	3.6	80.5	26700	6.07
7	**2**/1.0	1.0	4.0	2.5	2.0	90.0	4.4	85.6	23600	4.55
8	**2**/1.0	1.0	4.0	2.5	4.0	90.2	5.3	84.9	22800	3.67

as a function of polymerization time. Curves A and B represent the total polymer yield derived from monomers **1** and **2**, respectively. For both monomers **1** and **2**, the total polymer yield increases with increasing polymerization time. However, the yield of the polymer **3** which is derived from monomer **1** reaches 96.0% within a very short reaction time (about 0.5 h) and then over the rest of the polymerization time (about 3.5 h) increases only from 96.0% to 98.9%. In contrast, the yield of the polymer **4** derived from the monomer **2** increases from 58.2% to 90.2% during 4 h reaction time. It is also important to note that at equal reaction times the yield of polymer **3** is always higher than that of the polymer **4.** These results demonstrate that the rate of polymerization of **1** is consistently higher than that of **2.** Therefore, under these polymerization conditions, the polymerizability of 4,4-di(1-naphthoxy)diphenyl sulfone (**1**) is higher than that of 1,5-di(1-naphthoxy)pentane (**2**).

The dependences of the polymer molecular weight of the soluble fraction versus the polymerization time are plotted in Figure 2. Curves A and B show the dependence of $\overline{M}_n$ on the polymerization time for monomers **1** and **2**, respectively. Both curves have a maximum of $\overline{M}_n$ at intermediary reaction times. At reaction times shorter than 1 h Curve B is higher than curve A. This trend reverses for reaction times longer than 2 h. This complicated molecular weight dependence on reaction time requires a quantitative analysis of the amount of the polymer gel at each polymerization time.

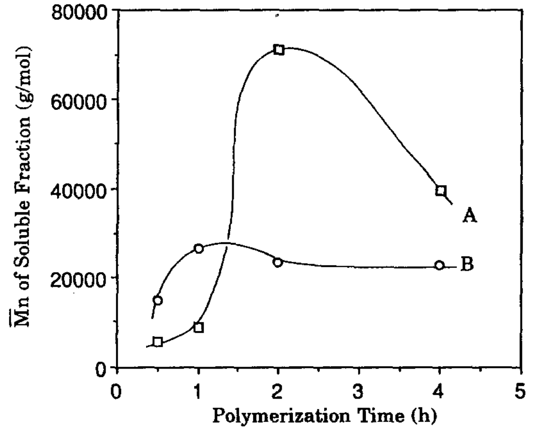


Figure 2. The dependence of number average molecular weight ($\overline{M}_n$) of soluble polymer fraction on the polymerization time: A) polymerization of 4,4'-di(1-naphthoxy)diphenyll sulfone; B) polymerization of 1,5-di(1-naphthoxy)pentane.

Figure 3 shows the yield of the polymer gel as a function of polymerization time. Curves A and B represent the amount of gel separated from the polymerization of **1** and **2** respectively. Curve A is much higher than Curve B at all polymerization times. Curve A also shows a sharp increase in the gel yield between 1 and 2 h. In contrast, Curve B

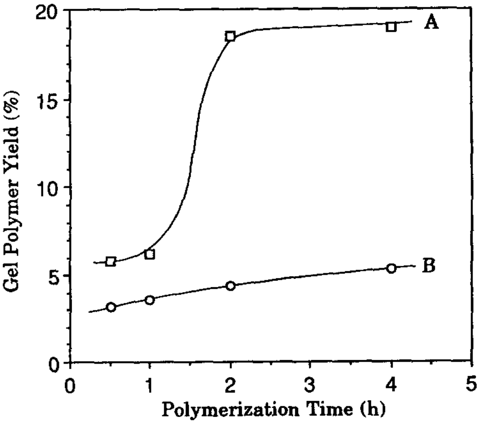


Figure 3. The dependence of the yield of the polymer gel on the polymerization time: A) polymerization of 4,4'di-(1-naphthoxy)diphenyll sulfone; B) polymerization of 1,5-di(1-naphthoxy)pentane.

increases only slightly as the reaction time increases. The higher initial gel content formed during the polymerization of **1** results in a lower $\overline{M}_n$ of the soluble fraction, since some of the high molecular weight fraction has already been transformed into the crosslinked insoluble polymer fraction. As the polymerization proceeds, the monomer concentration decreases and the polymer is first branched and subsequently crosslinked by the reaction of the reactive growing chain on the polymer backbone units. This effect determines that the $\overline{M}_n$ of soluble fraction will decrease after reaching a maximum. This maximum corresponds to the branched polymer before the gel point. In fact, this trend has been experimentally observed as shown in Figure 2.

The dependence of the amount of soluble polymer fraction on the polymerization time is presented in Figure 4. Curves A and B refer to the soluble fractions of polymer **3** and polymer **4** respectively. Curve B increases dramatically as the reaction time varies from 0.5 to 2 h. A slight decrease follows afterwards. Curve A increases slightly between 0.5 and 2 h, followed by a drop of about 10% in the polymer yield. These variations are accordingly caused by the different amount of polymer gel formed (Figure 3).

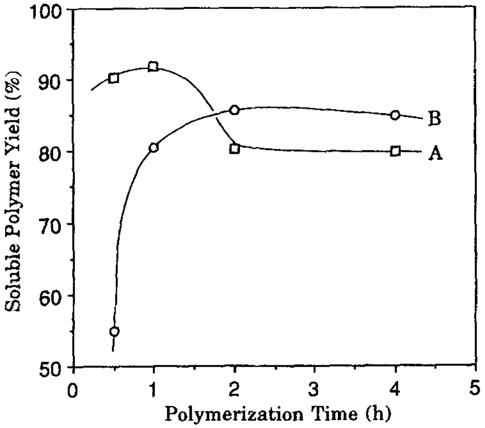


Figure 4. The dependence of the yield of the soluble polymer fraction on the polymerization time: A) polymerization of 4,4'di-(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-di(1-naphthoxy)pentane.

The $\overline{M}_n$ of the soluble fraction is plotted as a function of the total polymer yield in Figure 5. Curves A and B refer to the $\overline{M}_n$ of polymer **3** and polymer **4** respectively. Curve A is covering only the range of the total polymer yields higher than 96.0%. This curve has a maximum on the $\overline{M}_n$-Polymer Yield plot. Curve B also reaches a maximum. These trends are expected from the $\overline{M}_n$ versus polymerization time plot (Figure 2), and are caused by the formation of polymer gel.

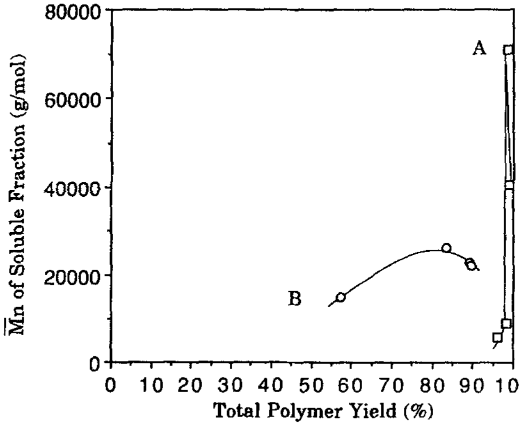


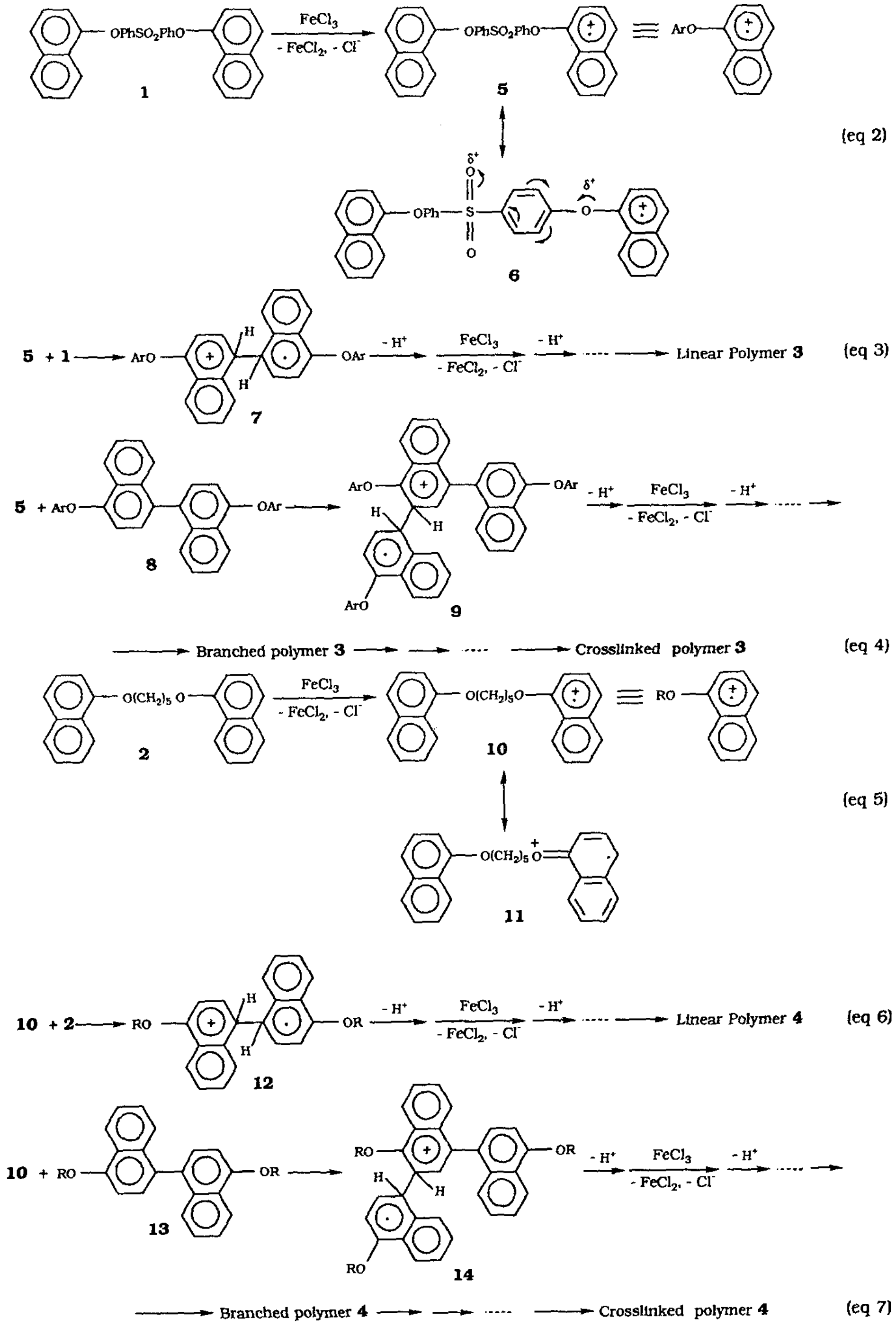
Figure 5. The dependence of number average molecular weight ($\overline{M}_n$) of the soluble polymer fraction on the overall polymer yield: A) polymerization of 4,4'di(1-naphthoxy)diphenyl sulfone; B) polymerization of 1,5-di(1-naphthoxy)pentane.

Although only in a relative way, both the $\overline{M}_n$ of the soluble polymer fraction and the yields of the overall, soluble and insoluble polymer fractions provide a reasonable estimate of the polymerizability of these two monomers. They suggest that the rate of the polymerization of 4,4'-di(1-naphthoxy)diphenyl sulfone (**1**) is higher than that of 1,5-di(1-naphthoxy)pentane (**2**).

A reasonable explanation for the observed difference between the polymerizability of these two monomers requires a brief discussion of the influence of molecular structure on the reactivities of both monomers and their corresponding growing species. Scheme II provides a parallel consideration of both monomers during this polymerization. The first step in the polymerization of **1** represents the oxidation of **1** to generate the radical-cation intermediate **5** (eq 2, Scheme II). The radical-cation **5** has two options. First, to function as an electrophile and therefore attack the monomer **1** with the formation of **7**, followed by a proton release, further oxidation, etc., to generate the linear polymer **3** (eq 3). Secondly, **5** may react with an internal 1,1'-binaphthyl unit **8** at the highest electron density position, i.e., C-2, leading to the intermediate **9**. The subsequent reactions of **9** first form a branched and then a crosslinked polymer **3**. The corresponding reactions of monomer **2** are shown in eq 5-7 from Scheme II. The difference between the polymerizability of monomers **1** and **2** is determined by the difference between the reactivities of the monomers and of the corresponding radical-cation growing species **5** and **10**. Monomer **2** is more reactive than monomer **1**, because the presence of an alkoxy group in monomer **2** makes its oxidation potential be lower than that of monomer **1**. The cation charge on the 1-naphthoxy ring in **5** derived from monomer **1** can only be partially delocalized onto the sulfonylphenoxy group as shown in the resonance structure **6** (eq 2). In contrast, the cation charge in the corresponding radical-cation **10** derived from monomer **2** can be completely delocalized on the alkoxy oxygen to form the oxonium species **11** (eq 5), which is unreactive. The radical of the resonance structure **11** is unreactive in radical-radical coupling reactions, beacuse the radical is resonanced stabilized due to its location at both allylic and benzylic position. Also the radical is located on a six-membered ring which is sterically unfavorable for radical-radical coupling reactions^2. The comparison of the growing species **5** and **10** indicates that **10** is more delocalized and thus more stable or unreactive than **5**. The rate of the propagation reactions (eq 3 and 6) are determined by both the reactivity or the nucleophilicity of the monomers and by the reactivity of the growing radical-cation species. The nucleophilcity of monomer **2** is higher than that of monomer **1**, while the reactivity of the radical-cation derived from monomer **1** is higher than that of monomer **2**. The experimental results have shown consistently higher overall polymer yield for the polymerization of monomer **1** (Figure 1) and also higher maximum $\overline{M}_n$ (Figure 2). Therefore the polymerizability of these monomers is predominantly determined by the reactivity of the growing species. This leads to a higher polymerizability of monomer **1** .

The difference between the polymerizability of the two monomers is determined by both the reactivity of the monomers and of their corresponding growing species. However, which of the reactivities dominates the polymerizability is determined by the relative differences between the reactivities of monomers and of the growing species. In the present case, the difference between the reactivity of the growing species is a dominant factor since the difference between the reactivity of the growing species is larger than that between the reactivity of the monomers. However, for the polymerization of 4,4'-di(1-phenoxy)diphenyl sulfone and 4,4'-di(1-phenylthio)diphenyl sulfone, the reactivity of the monomer determines the overall polymerizability since the difference between the reactivity of the growing species is smaller than that between the reactivity of the monomers.

The difference between the polymer gel content reflects the selectivity of the respective growing species. The growing species **5** derived from monomer **1** has higher reactivity than that of **10** derived from monomer **2**. Therefore, the radical-cation **5** should have a lower selectivity than the radical-cation **10**. The monomers **1** and **2** and the chain ends of their polymers are more nucleophilic than the internal 1,1'-binaphthyl unit from **8** or **13**. This is due to the presence of the 4-position of the naphthalene unit, which has the highest electron density, in both monomers **1**, **2**, and at the chain ends of a polymer



Scheme II. The radical-cation polymerization mechanism for the polymerization of 4,4'-di(1-naphthoxy)diphenyl sulfone and 1,5-di(1-naphthoxy)pentane.

molecule. The 4-position of the naphthalene unit is not available in compounds **8** and **13** and therefore, decreases the probability of these reactions. The 2-positions in structures **8** and **13** are also sterically hindered by the 1-phenoxy group (in **8**) or 1-alkoxy group (in **13**) by comparison with the 4-positions from the monomers **1** and **2** and from the chain ends of the corresponding polymers. These two factors determine that the formation of linear polymers is kinetically favored versus the generation of branched and subsequently crosslinked polymer fractions. The polymerization of monomer **1** has produced higher contents of polymer gel than that resulted from the polymerization of monomer **2**. This demonstrates that the growing species **5** derived from monomer **1** is less selective than that of **10** derived from monomer **2**. The experimental observation of polymer gel content also suggests that the growing species **5** is more reactive than the growing species **10**.

CONCLUSIONS

Under identical experimental conditions, the polymerization of 4,4'-di(1-naphthoxy)diphenyl sulfone (**1**) produced polymers of higher overall yield and higher number average molecular weight (M_n) than those resulted from the polymerization of 1,5-di(1-naphthoxy)pentane (**2**). The polymerizability of monomer **1** is higher than that of monomer **2**. This behavior is predominantly due to the higher reactivity of the radical-cation growing species derived from monomer **1**. The polymer gel content is determined by the selectivity of the growing species. The consistently higher polymer gel content obtained during the polymerization of monomer **1** also suggests that the radical-cation growing species derived from monomer **1** are more reactive than those derived from monomer **2**.

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REFERENCES

1. V. Percec and H. Nava , *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 783(1988).
2. V. Percec, J. H. Wang and Y. Oishi, *J. Polym. Sci. Polym. Chem. Ed.*, submitted.
3. R. Scholl and C. Seer, *Ber.*, **55**, 330(1922).
4. A.T. Balaban and C. D. Nenitzescu, in *Friedel-Crafts and Related Reactions*, Vol. II, Part 2, G. A. Olah, Ed., Interscience, New York, **1964**, p. 979.
5. R. G. Feasey, A. Turner-Jones, P. C. Daffurn and J. L. Freeman, *Polymer*, **14**, 241(1973).

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