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Poly(aryl ether ketone) Block and Chain-Extended Copolymers. 1. Preparation and Characterization of a New Class of Functional Poly(aryl ether ketone) Oligomers

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ABSTRACT: A series of poly(aryl ether ketone) (PAEK) oligomers with controlled molecular weights and end groups has been prepared via the Friedel–Crafts reaction of terephthaloyl chloride with diphenyl ether in the presence of either *p*-fluorobenzoyl chloride or fluorobenzene as the chain-terminating agents. The *p*-fluorobenzoyl chloride route is preferred, and the reaction is carried out in 1,2-dichloroethane, at 20–30 wt % solids, in the presence of a 30–40 mol % excess of aluminum chloride. A troublesome side reaction involving alkylation of the benzene rings is minimized under these conditions and is further minimized by the addition of a complexing agent. The oligomers were characterized by fluorine content, ^{13}C NMR, laser desorption–mass spectrometry, and GPC, which proved to be a powerful tool for the determination of purity. The fluorine contents agreed well with calculated values indicating a high degree of difunctionality.

Introduction

Crystalline poly(aryl ether ketones) (PAEK's) are a family of high-temperature engineering thermoplastics with an excellent combination of physical, thermal, and mechanical properties and solvent resistance characteristics. The literature cites two main synthetic routes to PAEK's: (1) the nucleophilic aromatic displacement of carbonyl-activated halides by phenoxide anions[1–3] and (2) the Friedel–Crafts electrophilic aromatic polyacylation condensation.[4–6]

Characteristically, this class of polymers is extremely insoluble due to their inherent high degree of crystallinity; hence, the preparation of PAEK oligomers with controlled molecular weight and functionality has not been described in the literature. PAEK oligomers are of interest since they are useful for the preparation of well-defined block and chain-extended copolymers, including those wherein both blocks are poly(aryl ether ketone) blocks. Note that, in those few instances where PAEK-containing block copolymers have been described, the synthetic approach generally consisted in preparing the segment of the more soluble component [e.g., of a poly(aryl ether sulfone)], followed by addition of the required PAEK coreactants and the in-situ formation of the final material.[7]

The preparation and characterization of a new class of functional poly(aryl ether ketone) oligomers are described in this report. In subsequent papers we will describe the synthesis of novel polymers based on these poly(aryl ether ketone) oligomers. Note that the processes described herein will also be useful to others because of their utility in the synthesis of new functionalized PAEK oligomers and novel polymers derived therefrom.

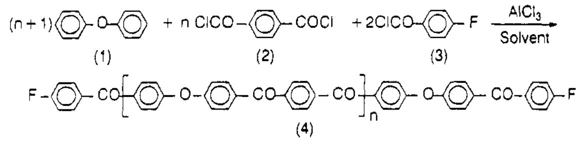
Results and Discussion

A. Preparation. The preparation involves the Friedel–Crafts polycondensation shown in Schemes I and II.

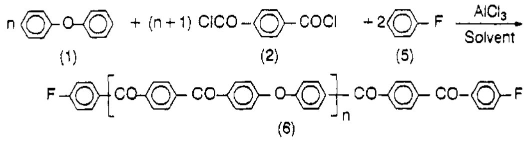
As can be seen, Schemes I and II differ in (1) the reagent used in excess (diphenyl ether in Scheme I versus terephthaloyl chloride in Scheme II) and (2) the terminating agent (*p*-fluorobenzoyl chloride in Scheme I versus fluorobenzene in Scheme II) employed to impart fluoroaromatic termination.

Oligomer 4 ($n = 1$) was also prepared by the sequence shown in Scheme III.

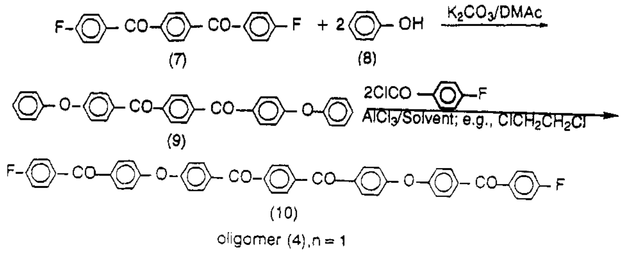
Scheme I
***p*-Fluorobenzoyl Chloride Route**



Scheme II
Fluorobenzene Route



Scheme III
Alternate Preparation of Oligomer 4 (n = 1)



The reactions described in Schemes I and II were studied in a number of solvents. In our initial experiments the use of aliphatic chlorinated solvents (methylene chloride or 1,2-dichloroethane) led to partially alkylated products; alkylation had an adverse effect on the properties of the polymers made from these oligomers. Due to the presence of the thermally labile alkyl groups, the resulting polymers were deficient in thermal stability; moreover, gelation, caused probably by the presence of reactive chlorinated impurities (vide infra), occurred when highly alkylated oligomers were polymerized.

The nature of some of the alkylated products formed in 1,2-dichloroethane (DCE) was elucidated by studying the model system benzoyl chloride/diphenyl ether/AlCl$_3$ in DCE.

In addition to the diadduct, 11, the corresponding monoadduct as well as a complex mixture of alkylated and chlorinated byproducts is formed in the above reaction.

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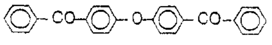
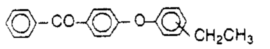
Materials **12**–**14** were identified via mass spectral (and liquid chromatography/MS) analysis. While the formation

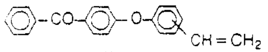


(11)

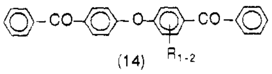
Diadduct



(12)



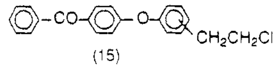
(13)



(14)

(mono- and dialkylated adduct)

of **13** is rather straighforward, **12** and **14** could be formed via product **15** by complexation with aluminum chloride



(15)

and rearrangement of the obtained carbonium ion (H$^-$ migration), followed by the aluminum chloride mediated transfer of hydride from DCE solvent.

It should be noted that all structures above are shown generically since the analysis method does not distinguish positional or other isomers.

A number of other typical Friedel–Crafts solvents were investigated and also proved inadequate. Thus, carbon disulfide gave heterogeneous reaction mixtures and was unacceptable because of its toxicity and flammability. *o*-Dichlorobenzene and trichlorobenzene, obvious candidates to replace the aliphatic chlorinated solvents, gave very complex reaction mixtures in which the reaction flask and stirrer were coated with polymer or where the polymer formed lumps of material. Because of the agglomeration problem, heating the reaction flask has to be performed very carefully to prevent charring the polymer. Moreover, model reactions (benzoyl chloride + diphenyl ether) have shown that termination by reaction of the acid chloride end groups with *o*-dichlorobenzene is probably taking place in the system. Byproducts were also observed with 1,1,2-trichloroethane and trichloroethylene. Reactions were very slow in nitrobenzene (at 50 °C); the use of sulfolane led to byproducts and to an incomplete reaction. Trichlorotrifluoroethane (FREON) with nitrobenzene or diethyl ether cosolvents gave heterogeneous systems and very little conversion. In summary, the study indicated that 1,2-dichloroethane was probably the most attractive reaction solvent. Therefore, an investigation with the goal of defining the experimental conditions which would minimize the formation of alkylated byproducts in this solvent was undertaken. As a first priority, however, a reliable and sensitive method whereby the degree of alkylation could be rapidly ascertained had to be developed.

Our studies have shown that the method of choice to determine the degree of alkylation was multistage pyrolysis gas chromatography/mass spectrometry (MPY-GC/MS). In a conventional pyrolysis technique the thermal degradation fragments of the polymer *and* any other volatiles (e.g., residual solvent) are indiscriminately volatilized; this approach may result in undesirable gas-phase reactions and generally leads to poor reproducibility and reliability. The aforementioned problem is conveniently circumvented by using MPY-GC/MS in which the sample is preheated under helium at a high enough temperature (150–200 °C) to vaporize all of the volatile components but below the pyrolysis temperature of the PAEK oligomers. Thus, residual solvents are removed, and the possibility of undesirable gas-phase reactions during pyrolysis is eliminated. The devolatilized sample is then inserted into the injection port of the gas chromatograph, rapidly heated to 700 °C, and held at this temperature for 5 min. The volatile components from the polymer degradation are collected in a liquid-nitrogen-cooled trap; they are subsequently separated via an appopiate GC column and analyzed by mass spectrometry.

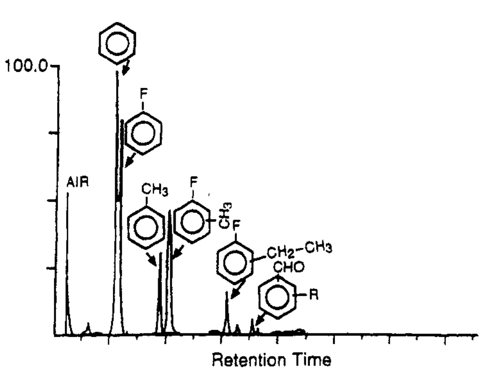
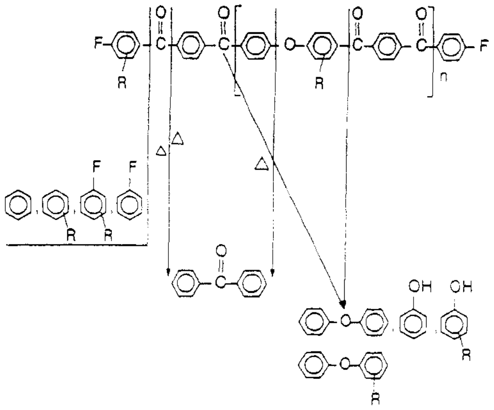


Figure 1. Selected portion of MPY-GC/MS chromatogram of a highly alkylated oligomer sample.

Scheme IV
Theoretical Fragmentation Pattern of an Oligomer



The theoretical fragmentation pattern of a typical oligomer is depicted in Scheme IV. A select portion of a MPY-GC/MS chromatogram of a highly alkylated oligomer sample is shown in Figure 1.

The relative degree of alkylation was first determined by adding the gas chromatographic peak heights of all the alkylated pyrolysis products and dividing by the weight of the sample (peak heights per milligram). In all cases investigated, the largest alkylated peak in the pyrogram corresponded to toluene; therefore, it was used to measure and compare the relative degree of alkylation. As a quality control test, a flame ionization detector was used. The precision of this technique was established by repeatedly analyzing the same sample over a period of time. The overall standard deviation was ±5%.

Using the above analytical tool as a guide, it was established that the preferred conditions for the preparation of high-quality PAEK oligomers in DCE via the *p*-fluorobenzoyl chloride route were % solids = 20–30 wt % (higher solid contents yielded highly viscous or gelatinous reaction mixtures that were difficult to handle) and $AlCl_3$ excess = 30–40 mol %.

Another approach whereby alkylation could possibly by suppressed was to use a complexation agent to moderate the reactivity of the $AlCl_3$. It was hoped that the complexation agent would deactivate the system sufficiently to prevent alkylation while still catalyzing acylation reactions. In our hands, the use of complexation agents such as nitromethane, lithium chloride, or sulfolane in DCE also gave materials with a lower degree of alkylation. It was preferred to use a mole ratio of complexation agent/COCl of >1.5, a solids content ≥20 wt %, and, when the

Table I
Effect of Process Options and Variables on Alkylation Levels in PAEK Oligomers Made in DCE

no.	Scheme	complexation agent	reaction time (h)/temp (°C)[a]	excess $AlCl_3$ (mol %)	solids (wt %)	alkylation (peak height of toluene/mg of sample)
1	I	sulfolane	17/25	50	18	13.9
2	I			100	30	17.2
3	I			100	10	22.0
4	I		17/25	30	17	21.9
5	II[b]		17/25	30	11	82.4

[a] All experiments were performed by stirring for 6 h at 0 °C plus as indicated. [b] Fluorobenzene (excess) was added after 6 h at 0 °C.

Table II
PAEK Oligomers[a]

no.	Scheme	n	excess of $AlCl_3$ (mol %)	complexation agent	mole ratio of CA[b]/COCl groups	solids (wt %)	% fluorine calcd	% fluorine found	RV[c] (dL/g)
1	I	2	40			28.3	3.74	3.76	
2	II	2	9.3	CH_3NO_2	2	23.7	4.12	3.96	
3	I	5	29.8			20.5	1.98	1.98	0.14
4	I	5	15	CH_3NO_2	1.71	20.8	1.98	1.93	0.15
5	I	10	15	LiCl	1.8	19.8	1.11	1.04	0.20
6	I	10	15.8	CH_3NO_2	1.88	20.0	1.11	1.05	0.23
7[d]	I	20	30			26.0	0.59	0.58	0.33

[a] The preparation of oligomer 4 (n = 1) via the sequence of Scheme III is given in the Experimental Section. [b] Complexation agent. [c] Reduced viscosity measured in concentrated H_2SO_4 at 25 °C (1 g/100 mL). [d] A mixture of isophthaloyl/terephthaloyl chlorides (5:95 molar) was used.

p-fluorobenzoyl chloride route was employed, an excess of $AlCl_3$, over the molar amount of the COCl groups and of the complexation agent of about 15 mol %.

Some alkylation results obtained in DCE under various experimental conditions are presented in Table I. Note the acceptable low degrees of alkylation obtained by Scheme I as opposed to the relatively high degree observed for example no. 5 (fluorobenzene route). Scheme II was not investigated in as much detail as Scheme I.

All of the reactions (with or without the complexation agent) were performed at 0–5 °C (1.5–6 h); prior to workup the reaction mixtures were often stirred at room temperature for 16–20 h. Note that for n = 2 DCE reactions performed via Scheme I were heterogeneous at low concentrations (solid contents of about 5 wt %); at high solid contents (Table II) the reaction mixtures were homogeneous. At higher n values the DCE reaction mixtures were heterogeneous regardless of the solids contents. Homogeneity was achieved, however, in the presence of the complexation agents.

A series of oligomers as well as the experimental conditions used for their preparation are listed in Table II. Fluorine analyses and reduced viscosities are also shown.

The results of the fluorine analyses show that the oligomers were of excellent quality. Furthermore, both the fluorine and the reduced viscosity data indicate that practically identical results are obtained in the presence or in the absence of the complexation agent.

The novel functional oligomers possessed a high degree of difunctionality and could be polycondensed under nucleophilic conditions with, for example, bisphenols or bisphenols and activated aromatic dihalides. High molecular weight chain-extended copolymers and PAEK/PAEK and PAEK/poly(aryl ether sulfone) block copolymers were prepared. These materials possess very attractive properties and will be discussed in subsequent papers.[8,9]

B. Characterization. In addition to fluorine analysis and measurement of reduced viscosities, the oligomers were also characterized by a number of other techniques including ^{13}C NMR and GPC. Chemical shifts were assigned based on the study of a large number of model compounds. As an example, the following chemical shifts were assigned to the various carbon atoms of oligomer 6 (n = 2).

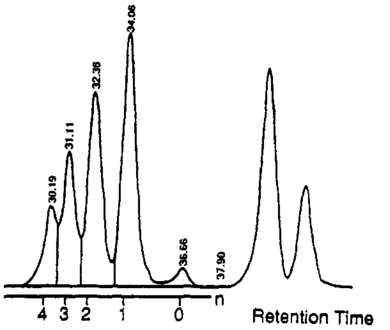
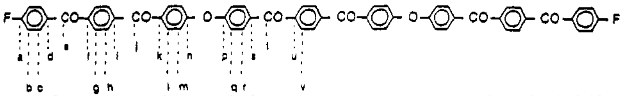


Figure 2. Gel permeation chromatogram of oligomer 4 (n = 2) polymer-grade material.

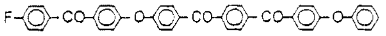


carbon atom	chemical shift (ppm)	carbon atom	chemical shift (ppm)
a	175.8, 171.7	l	141.8
b	119.3, 118.9	m	121.5
c	142.2	n	167.7
d	125.8	p	167.7
e	206.2	q	121.5
f	137.1	r	~141.8
g	133.6	s	125.8
h	133.6	t	204.8
i	137.1	u	~137.0
j	204.8	v	133.6
k	~125.8		

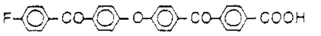
The characterization method of greatest practical value was gel permeation chromatography (GPC). The gel permeation chromatogram of oligomer 4 (n = 2) is shown in Figure 2. It was obtained by using a metastable solution of the material in a mixture of trichloroacetic acid/1,1,2,2-tetrachloroethane; methylene chloride was the mobile phase, and the apparatus was a Waters GPC II liquid chromatograph equipped with a UV detector. The optimum column arrangement consisted of two Waters μ-Styragel columns in series: one of 500-Å pore size and the other of 1000-Å pore size. Detection was done by UV (254 nm).

The chromatogram shows that the material is a mixture of low molecular weight oligomers and polymers. There is clear separation of the $n = 0$ through $n = 3$ oligomers. The $n = 4$ oligomer is not resolved from the $n = 5$ and higher oligomers and should be considered as a composite of the higher oligomers.

Note that the chromatogram of Figure 2 corresponds to a "good" sample of oligomer 4 ($n = 2$), i.e., one having adequate functionality and suitable for polymerization. Other oligomer samples gave GPC chromatograms having a shoulder on the peak corresponding to the $n = 1$ oligomer or having a peak midway between the peaks corresponding to the $n = 0$ and $n = 1$ oligomers. The shoulder and the additional peak were shown to be due to the side products A and B. These side products were identified by negative ion mass spectroscopic analysis of low molecular weight pyridine extracts of the impure oligomers. Further confirmation was obtained using laser desorption/mass spectrophotometric techniques. The latter, upon analysis of good (polymer-grade) oligomer (Figure 2), showed mass ions for $n = 0$ to $n = 4$. Similar investigations of bad oligomers showed additionally mass ions for incompletely end-capped materials. The presence of these two impurities is detrimental to oligomer quality. The origin of these impurities is easy to visualize: they could be due to mischarge of the reactants, to the use of impure reactants, or to insufficient reaction time.



A



B

Thus, as far as the quality of the oligomers is concerned, GPC is a very powerful and useful monitoring tool.

Conclusions

The preparation and characterization of a new class of aromatic poly(aryl ether ketone) oligomers are described. The materials are formed via the Friedel–Crafts reaction of terephthaloyl chloride with diphenyl ether in the presence of either p-fluorobenzoyl chloride or fluorobenzene as the chain-terminating agent. Optimum preparative conditions using the p-fluorobenzoyl chloride route involve carrying out the reaction in DCE, at 20–30 wt % solids, in the presence of an excess of aluminum chloride (30–40 mol %). Good quality oligomers were also obtained using a complexation agent in combination with $AlCl_3$ in DCE as the solvent. The experimentally determined fluorine contents of the obtained oligomers were in excellent agreement with their calculated values, indicating a high degree of difunctionality. The oligomers were further characterized by ^{13}C NMR, laser desorption/mass spectrometry, and GPC. The latter is a powerful analytical tool for the determination of the purity of these materials.

Experimental Section

a. Preparation of Oligomer 4 ($n = 2$; Scheme I). A 500-mL, four-neck, round-bottomed flask equipped with a mechanical stirrer (Teflon blade), nitrogen inlet, thermometer, solids addition funnel, and gas outlet to a NaOH scrubber was purged with dry nitrogen and charged with 190 mL (240 g) of 1,2-dichloroethane, 21.25 g (0.1340 mol) of 4-fluorobenzoyl chloride, 34.04 g (0.200 mol) of diphenyl ether, and 27.20 g (0.1340 mol) of terephthaloyl chloride. The addition funnel was charged with 75.04 g (0.5628 mol) of high-purity aluminum chloride. The solution was cooled to <5 °C (ice water bath), and the aluminum chloride was added at a rate such that the reaction temperature did not rise above 5 °C. The reaction mixture was stirred with cooling for 6 h, *during which time it became homogeneous.* The viscous reaction mixture was pumped slowly using nitrogen pressure, through a $^3/_8$-in. polyethylene cannula into a 2-L, three-neck, round-bottomed flask (equipped with a heating mantle, mechanical stirrer, Claisen head, thermometer, Dean–Stark trap, and condenser) containing 400 mL of water at 85 °C. Dichloroethane was removed by distillation during the transfer. Once the transfer was complete, the slurry was heated to 95 °C, kept 15 min to remove traces of dichloroethane, and then allowed to cool to 45 °C. The crude product was recovered by vacuum filtration, rinsed on the filter with methanol, then with deionized water until the rinsings were neutral, and then again with methanol, and allowed to dry in air.

The product was then added to a solution of 9 mL of concentrated HCl in 155 mL of methanol, and the resulting slurry was heated at reflux for 90 min with stirring. The product was recovered by vacuum filtration, rinsed with deionized water until the rinsings were neutral and then rinsed with methanol, and allowed to dry in air. The air-dried product was heated overnight under house vacuum ($\sim$28 Torr) at 100 °C to give 63.8 g (94%) of the oligomer. Anal. Calcd: C, 78.10; H, 3.97; O, 14.19; F, 3.74. Found: C, 78.06; H, 4.07; O, 14.08; F, 3.76. Oligomers 3–7 (Table II) were prepared in a similar manner.

b. Preparation of Oligomer 4 ($n = 1$; Scheme III). b.1. Condensation of 1,4-Bis(p-fluorobenzoyl)benzene with Phenol. Into a 1-L, four-neck flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean–Stark trap, and reflux condenser were placed 37.64 g (0.4 mol) of phenol, 64.46 g (0.2 mol) of 1.4-bis(p-fluorobenzoyl)benzene, and 34.55 g (0.25 mol) of K_2CO_3. The apparatus was evacuated four times to remove all air (dry argon flush); 150 mL of toluene and 450 mL of DMAc were then added. The mixture was heated gradually, with stirring, to 155 °C (45 min), at which temperature distillation of toluene/H_2O began; it lasted 2 h. The reaction mixture was kept at 155 °C for an additional 3 h. The temperature was then raised to 165 °C (10 min) and kept at that level for 15 min. The reaction mixture was cooled and coagulated in a solution of 25 mL of concentrated HCl in 3 L of water; the obtained suspension was stirred at room temperature for 30 min. The precipitate was filtered and dried under house vacuum ($\sim$28 Torr). Recrystallization (2×) from chlorobenzene gave the condensation product, 1,4-bis(p-phenoxybenzoyl)benzene (mp = 215–215.5 °C), in a yield of 87%.

b.2. Friedel–Crafts Reaction of 1,4-Bis(p-phenoxybenzoyl)benzene with p-Fluorobenzoyl Chloride. A 1-L, four-neck flask equipped with a mechanical stirrer (Teflon blade), nitrogen inlet, thermometer, solids addition funnel, and gas outlet to a NaOH scrubber was purged with nitrogen and charged with 625 mL of 1,2-dichloroethane (DCE), 47.05 g (0.1 mol) of 1,4-bis(p-phenoxybenzoyl)benzene, and 34.88 g (0.22 mol) of p-fluorobenzoyl chloride. The solids addition funnel was charged with 72.80 g (0.546 mol) of $AlCl_3$. The flask and its contents were cooled to 0 °C (ice water bath) and the aluminum chloride was added at a rate such that the reaction temperature did not rise above 5 °C. The reaction mixture was then stirred at 0–5 °C for 6 h. At the end of that period it was heterogeneous. The reaction mixture was poured into a solution of 100 mL of concentrated HCl in 3 L of water and heated to reflux to remove all DCE. The suspension was filtered hot, and the precipitate was rinsed with hot water. The precipitate was then washed in a blender twice with distilled water and twice with methanol. The crude product was obtained in a yield of 97%. Recrystallization from DMAc yielded a material melting at 315–315.5 °C. MPY-GC/MS results were 7.3 and 6.2 peak height of toluene/mg of sample for the crude and recrystallized product, respectively. Anal. Calcd: C, 77.30; H, 3.96; F, 5.32. Found: C, 77.24; H, 4.41; F, 5.22.

c. Preparation of Oligomer 6 ($n = 2$; Scheme II). The apparatus used in the preparation described in section a was charged with 152 mL (192 g) of 1,2-dichloroethane, 19.53 g (0.3200 mol) of nitromethane, 18.25 g (0.1072 mol) of diphenyl ether, and 32.48 g (0,1600 mol) of terephthaloyl chloride. The addition funnel was charged with 93.5 g (0.7001 mol) of aluminum chloride. The solution was cooled (ice water bath) to <5 °C, and the aluminum chloride was added at a rate such that the reaction temperature did not rise above 5 °C. The mixture was stirred for 20 min, and then the solids addition funnel was replaced with a regular addition funnel, which was charged with 10.30 g (0.1072 mol) of fluorobenzene. The fluorobenzene was added intermittently over a period of 90 min. The cooling bath was removed, and the mixture was stirred at room temperature for 20 h, during which time it became homogeneous. The product was worked up using the procedure described in section a. Anal. Calcd: F, 4.12. Found: F, 3.96.

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(9) Part 3: Botkin, J. H.; Cotter, R. J.; Matzner, M.; Kwiatkowski, G. T. *Macromolecules*, following paper in this issue.