Macromolecules **1996,** *29,* 1085−1087

Encapsulation of Emissive Polymers within a Fluorinated Matrix

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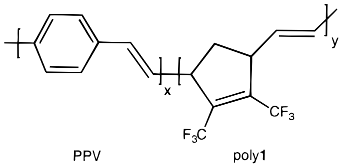
Received September 21, 1995
Revised Manuscript Received November 27, 1995

There is a considerable need to develop and fine-tune synthetic methods to prepare block copolymers composed of segments of specific and distinct functions.[1] Especially challenging are protocols capable of adjoining two homopolymers containing very different functionalities in a stereoregular manner. Additional considerations are required when one of the partners is conjugated. Conjugated chains are insoluble and intractable, as a result of their rigid delocalized structure, and their preparation proceeds via a precursor material that must ultimately be transformed to the target structure.[2] Conditions for the final elimination reactions are typically elevated temperatures and/or the use of base or acid catalysts that may introduce oxidative impurities or defects. In the case of conjugated emissive polymers, oxidative impurities are effective exciton traps that significantly abate important useful properties such as photoluminescence or electroluminescence efficiency.[3] Procedures that circumvent harsh conversion conditions therefore have a tendency to produce higher quality material.

It occurred to us that a potentially interesting hybrid material would be a block copolymer containing poly(*p*-phenylenevinylene) (PPV) and *trans*-*syndiotactic*-poly(2,3-bis(trifluoromethyl)norbornadiene) (poly**1**).



PPV poly1

PPV$_x$-*block*-poly1$_y$

PPV is of current worldwide interest as it exhibits electroluminescence and can be implemented as an emissive material in light-emitting diodes.[4] The fluorinated section has, after poling, an unusually high relaxed dielectric constant and demonstrates pyroelectric behavior.[5] Both homopolymers are accessible via ring-opening metathesis polymerization (ROMP) but require different molybdenum-based Schrock-type initiators.[6] PPV is derived from the *cis*-specific living ROMP of 9-((*tert*-butyldimethylsilyl)oxy)-[2.2]-paracyclophan-1-ene (**2**), which works only when very reactive initiators, such as Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2,6-diisopropylphenyl), are used.[7] Conversion of poly**2** to PPV requires two additional steps, deprotection to poly(9-hydroxy-[2.2]-paracyclophan-1-ene) and finally dehydration using a catalytic amount of HCl. Poly**1** requires an all-*trans*, highly tactic, stereochemistry to maximize its pyroelectric properties.[5] For this purpose, the less reactive but *trans*-specific Mo(NAr)(CHCMe$_2$Ph)(OCMe$_3$)$_2$ works well, producing poly**1** with a 92% tactic content.

The alkoxide-ligand exchange studies of Feast and Gibson suggested that it should be possible to convert quantitatively any Mo(NAr)(CHR)[OCMe(CF$_3$)$_2$]$_2$ species, where CHR is a propagating alkylidene, to Mo(NAr)(CHR)(OCMe$_3$)$_2$ by simple addition of excess LiOCMe$_3$.[8] The equilibrium in this exchange predominantly favors ligation of the more electron-donating alkoxide and is driven by the electrophilic nature of the metal center. Since these polymerizations are living, the propagating species, after consumption of monomer, can be viewed simply as alkylidenes where R represents a polymer chain and which may undergo ligand exchange reactions at molybdenum. A second monomer would then be incorporated, but with the kinetic specificity of the modified metal center.

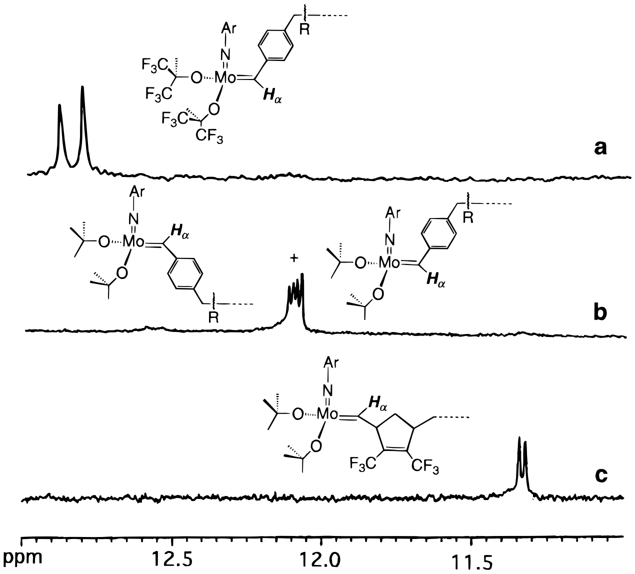


Figure 1. ^{1}H NMR (C_6D_6) spectra in the alkylidene region for the reaction of (a) [(CF$_3$)$_2$MeCO]$_2$Mo(NAr)(CH$_\alpha$poly**2**$_{20}$), (b) [Me$_3$CO]$_2$Mo(NAr)(CH$_\alpha$poly**2**$_{20}$), and (c) [Me$_3$CO]$_2$Mo(NAr)(CH$_\alpha$-poly**1**$_{50}$-*block*-poly**2**$_{20}$).

We have successfully applied this strategy to the preparation of PPV$_{20}$-*block*-poly**1**$_y$ (y = 50, 100, 200, etc.), and the detailed sequence of steps is shown in Scheme 1.[9] Adding **2** to Mo(NAr)(CHR)[OCMe(CF$_3$)$_2$]$_2$ results in living *cis*-poly**2** (**A** in Scheme 1). At this stage, 3−4 equiv of LiOCMe$_3$ are added which completely replace their fluorinated counterparts on molybdenum to generate a new propagating species **B**. The alkylidene and imido ligands are left unperturbed by this alkoxide exchange. ^{1}H NMR spectroscopy lends itself well to monitor the changes at the metal and the signals of MoCH$_\alpha$ are especially diagnostic. For example, the spectrum in the alkylidene region of the reaction mixture resulting from addition of 20 equiv of **2** to Mo(NAr)(CHR)[OCMe(CF$_3$)$_2$]$_2$ is shown in part a of Figure 1. The two singlets at 11.80 and 11.89 ppm are due to the propagating benzylidene in living Mo(NAr)[OCMe(CF$_3$)$_2$]$_2$-poly**2** (two signals are observed due to the head-to-head and head-to-tail isomers). A significant upfield shift of the signals occurs after addition of LiOCMe$_3$ but, instead of two, now four signals are detected. The frequency range of the new alkylidene signals is consistent with previously characterized benzylidene complexes of the type Mo(NAr)(OCMe$_3$)$_2$(CHPh). We are unsure at the present time as to why the number of signals increases after alkoxide addition. Our current thinking is that the signals arise as a result of head-to-head and head-to-tail isomerism and *syn* and *anti* rotamers.[10] These new alkylidenes, while stable for

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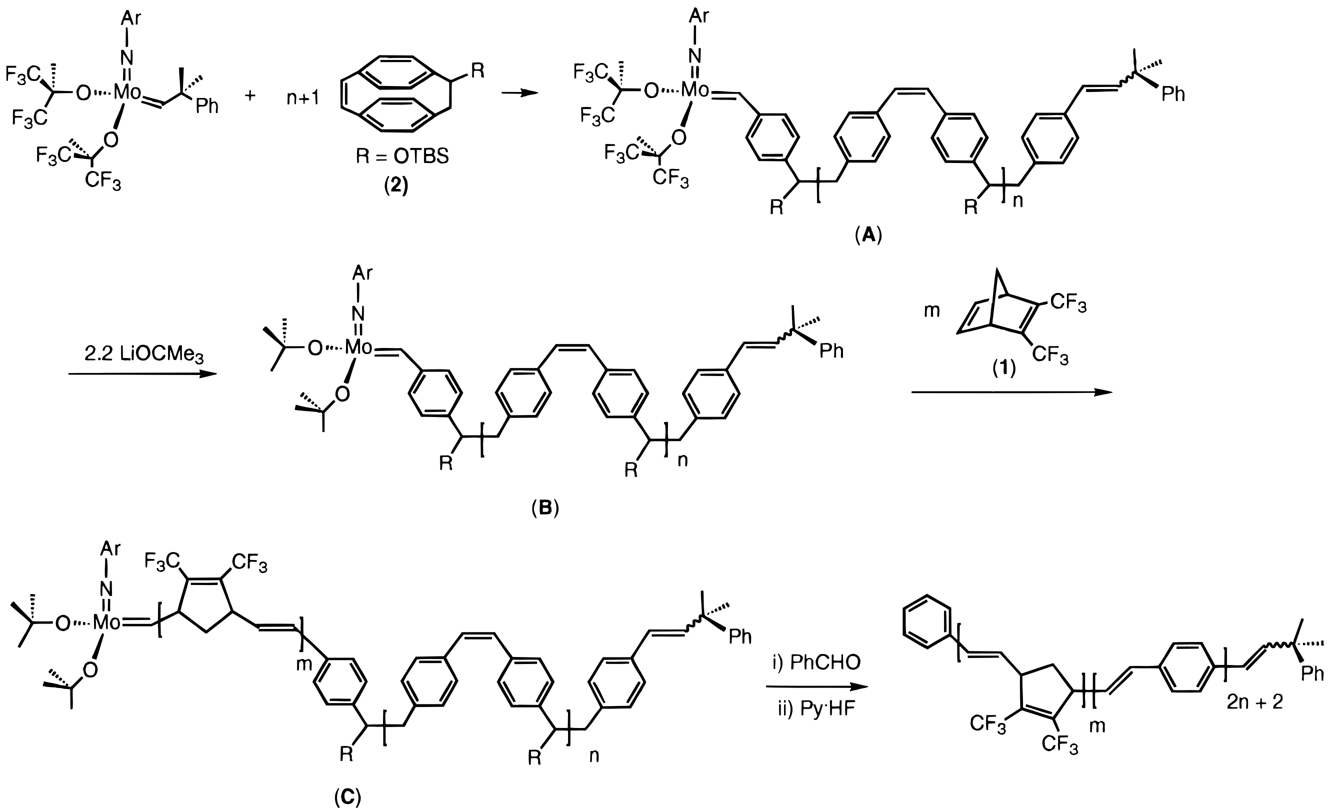
Scheme 1



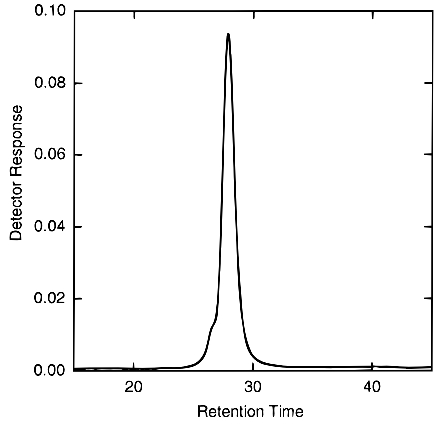


Figure 2. GPC trace ($CHCl_3$, vs polystyrene standards) of poly$\mathbf{2}_{10}$-*block*-poly$\mathbf{1}_{200}$.

several hours at room temperature if kept under nitrogen, are reactive enough to initiate the polymerization of **1**. After addition of 50 equiv of **1**, the alkylidene resonance is a doublet centered at 11.42 ppm (part c of Figure 1) characteristic of living $Mo(NAr)(OCMe_3)_2$-poly**1**-*block*-poly**2** (**C** in Scheme 1).

Any failure in the transformation of propagating species affects the final molecular weight distribution. Incomplete conversion and/or slow ligand exchange will cause a broadening of the polydispersity (PDI) since propagating species of different activities would be present, each consuming the monomer at different rates. Alternatively, any termination of metal sites during alkoxide exchange will result in the presence of a lower molecular weight component. As shown in Figure 2, a unimodal molecular weight distribution is observed for poly$\mathbf{2}_{10}$-*block*-poly$\mathbf{1}_{200}$ with a polydispersity value (1.08) that approaches the Poisson limit.[11] Furthermore, the absorption spectrum of the GPC eluent shows an

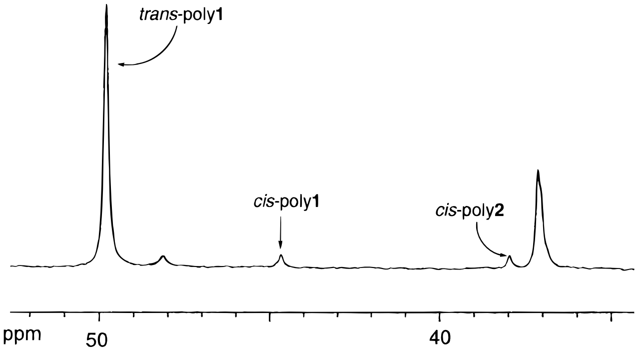


Figure 3. ^{13}C NMR (acetone-d_8) spectrum in the 35−50 ppm region of poly$\mathbf{2}_{10}$-*block*-poly$\mathbf{1}_{200}$.

absorption maximum at approximately 300 nm throughout the peak area, confirming the presence of stilbene segments in the entire sample.

While the GPC results confirm the absence of termination or chain transfer, it is the ^{13}C NMR spectrum of the polymers that establishes the stereoregulation change. Figure 3 confirms the stereochemistry as *cis*-poly$\mathbf{2}_{10}$-*block*-*trans*-*syndiotactic*-poly$\mathbf{1}_{100}$,[5] with the signal at 38.0 ppm corresponding to the unsubstituted benzylic sites in *cis*-poly**2** while that at ~49.8 ppm is due to the allylic carbons in *trans*-*syndiotactic*-poly**1**. Contribution from other isomers is estimated at less than 5%.

The final step, conversion of the poly**2** segment to PPV, requires a slight modification of our original procedure as HCl treatment, useful in the case of the homopolymer, degrades the fluorinated block. Instead, we have found that a slight excess of pyridine·HF (relative to **2**) in tetrahydrofuran (THF) cleanly converts *cis*-poly$\mathbf{2}_{10}$-*block*-*trans*-poly$\mathbf{1}_{200}$ to PPV_{20}-*block*-*trans*-poly$\mathbf{1}_{200}$.[12] This material is soluble in CH_2Cl_2 and trifluorotoluene and displays absorption and emission

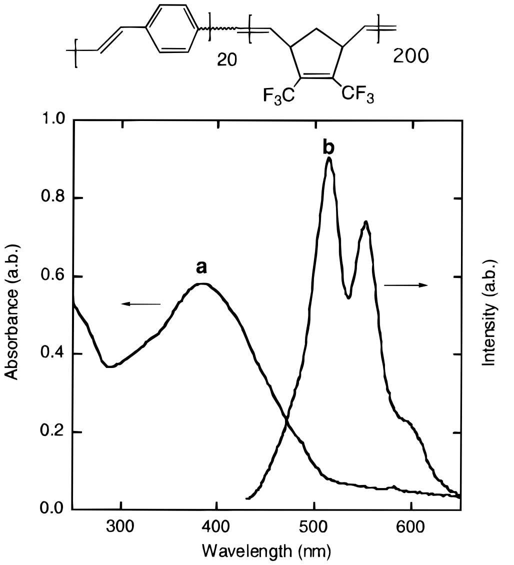


Figure 4. (a) Emission ($\lambda_{\mathrm{excitation}}$ = 400 nm, film on quartz plate) and (b) absorbance spectra of PPV_{20}-*block*-poly$\mathbf{1}_{200}$.

spectra entirely consistent with previously characterized PPV (Figure 4).

In summary, we have successfully encased short emissive PPV sequences of controlled length and polydispersity within a fluorinated polymer matrix. The synthesis of this architecture required an *in situ* change of stereoregulation promoted by ligand exchange. Such stereochemical control demonstrates nicely the flexibility of well-defined transition metal catalysts and may prove to be general in cases where the propagating species is stable and facile ligand-sphere modification reactions are possible. We note that PPV_{20}-*block*-poly$\mathbf{1}_{200}$ is soluble in a variety of organic solvents and that the fluorescence quantum yield of the PPV segments decreases less rapidly than PPV alone.[13] Further studies on the photooptical properties of these materials are under way.

Acknowledgment. The authors gratefully acknowledge the Office of Naval Research and NSF (Grant CHE-9120001) for partial support of this work and Yi-Jun Miao for useful discussions.

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(8) Feast, W. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.

(9) Representative procedure: The initiator (10 mg) and monomer **2** (89 mg, 20 equiv) are dissolved in rigorously dry toluene (10 mL) and allowed to react for 10 h. After this period, $LiOCMe_3$ (3−4 mg, approximately 3 equiv) in THF (~1 mL) is added to the polymerization solution and reacted for 30 min. Finally, **1** (602 mg, 200 equiv) in toluene (5 mL) is added and the reaction quenched after 5 h using benzaldehyde. Precipitation of the resulting solution into either methanol or pentane followed by removal of volatiles yields 620 mg (~90%) of *cis*-poly$\mathbf{2}_{20}$-*block*-*trans*-poly$\mathbf{1}_{200}$.

(10) Rotamers are well known in this class of initiators; see: Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

(11) The slight contribution by the high molecular weight component observed in Figure 2 has precedent in polymers from ROMP reactions. It appears to arise from a postpolymerization bimolecular dimerization initiated by dioxygen; see: Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L.; Mitchell, J. P. *Polymer* **1992**, *33*, 872.

(12) Representative procedure: A dilute solution of *cis*-poly$\mathbf{2}_{20}$-*block*-*trans*-poly$\mathbf{1}_{200}$ (90 mg) in THF (100 mL) was treated with 131 mg of pyridine•HF (5 equiv) and allowed to react for 3 days. During this period the solution turns the characteristic yellow-green color of PPV. The solvent is removed under vacuum and the resulting yellow solid is extracted four times with 50 mL of CH_2Cl_2 (or trifluorotoluene), the resulting solution is concentrated to approximately 5 mL, and the product (44 mg) is obtained as a yellow-green powder by precipitation into pentane (100 mL) and centrifugation. All manipulations are carried out under nitrogen. All spectroscopic data (^1H and ^{13}C NMR, IR, and UV−vis spectroscopies) are consistent with the formulation PPV_{40}-*block*-*trans*-poly$\mathbf{1}_{200}$.

(13) It seems that the fluorinated polymer protects the PPV segments, slowing down oxidation of the chains: Renak, M.; Bazan, G. C., unpublished results.

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