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# Stereoselective Polymerization of [2.2]Paracyclophan-1-ene

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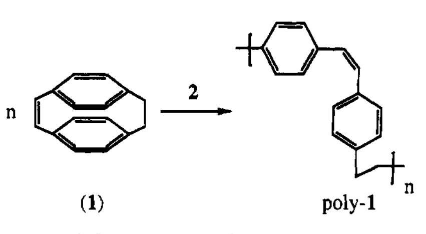
Ring-opening metathesis polymerization (ROMP) of cyclic olefins using well-defined initiators provides a method of preparing polymers in which olefins are an integral part of the polymer backbone.[1] Progress in the field of initiator design and synthesis has produced several complexes that are capable of effecting such polymerizations in a living fashion[2] with a range of activities, tolerance to functionalities, and stereoselectivity.[3] Monomers typically must contain a significant amount of ring strain energy, important in forcing the entropically disfavored polymerization to completion as well as for kinetic reasons. This energetic prerequisite has restricted monomers largely to norbornene derivatives, primarily because of their ease of preparation via electrocyclic reactions.[4]

A class of molecules that meets the monomer requirements is paracyclophane derivatives such as [2.2]paracyclophan-1-ene (1).[5,6] A simple two-step procedure from commercially available paracyclophane yields adequate amounts of 1 for polymerization studies.[7] Reactivity studies revealed that many ROMP catalysts (based on W and Mo), in a variety of solvents, polymerized 1 to insoluble material, consistent with reported polymerizations of this monomer.[8] Use of $Mo(NAr)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ (Ar = 2,6-diisopropylphenyl) (2)[2d] in toluene proved to be an exception, producing soluble poly([2.2]paracyclophan-1-ene) (poly-1).[9] A singlet, attributed to $H_\alpha$ of the new propagating alkylidene, was observed by $^1H$ NMR spectroscopy at 12.84 ppm ($C_6D_6$, 25 °C), the intensity of which grows at the expense of 2 as the reaction proceeds to completion. This new alkylidene is stable for weeks in solution under a nitrogen atmosphere and in the absence of light, but it is completely consumed by addition of norbornene (NBE) and is replaced by the alkylidene signal (12.77 ppm, $C_6D_6$, 25 °C) observed when NBE is added to 2, i.e., living poly(NBE). These observations, together with the narrow polydispersities of the isolated polymers, are consistent with a living polymerization process.



Two aspects of the propagation process are noteworthy. First, relative to norbornene derivatives, the polymerization is slow (*vide infra*), with consumption of 100 equiv. of 1 requiring over 18 h at room temperature (0.01 M initiator in toluene). The slower propagation rate is a manifestation of the expected congestion between the ortho hydrogens in 1 and the bulky ligands on molybdenum. Steric interactions of this type are likely to be less severe in typical monomers derived from norbornene because of their smaller size.[1c] Additionally, propagating poly-1 is a substituted benzylidene, a type of species which is relatively unreactive.[10] A second notable feature is the stereoselectivity with which poly-1 is produced (~98% *cis* by $^1H$ and $^{13}C$ NMR analysis; Figure 1).[11] Photolysis or treatment with a catalytic amount of iodine (<1%) results in precipitation of the polymer presumably via isomerization to the less soluble *trans* isomer. Additional evidence for this process is provided by FTIR analysis of poly-1 films which display, upon irradiation, a decrease in the intensity of the signal at 880 $cm^{-1}$ due to the out-of-plane vibration of the *cis*-vinylene C–H bond and simultaneous increase of the absorbance at 963 $cm^{-1}$ due to the analogous vibration in the *trans* isomer.[12]

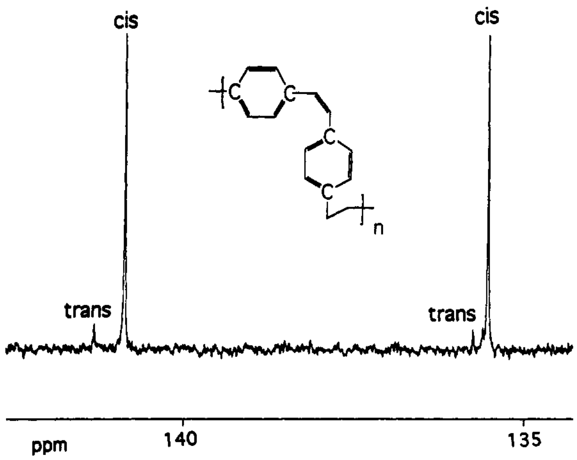


**Figure 1.** $^{13}C$ NMR ($C_6D_6$) spectrum of poly([2.2]paracyclophan-1-ene) in the aromatic region.

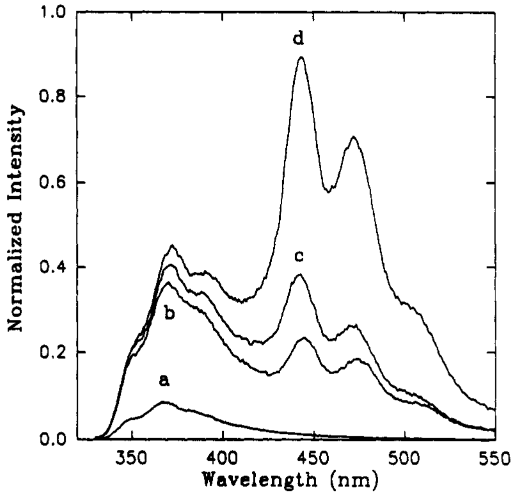


**Figure 2.** Dependence of fluorescence emission ($\lambda_{excitation}$ = 330 nm) spectra of poly-1 on irradiation time: (a) 0 min, (b) 2 min, (c) 4 min, (d) 10 min.

Structurally, poly-1 is attractive since it is essentially a polymer composed of linked *cis*-stilbene units, i.e., a stereoregular polychromophore. The photoluminescence ($\lambda_{excitation}$ = 330 nm) of a solution of poly-1 in $CHCl_3$ is dependent on irradiation time (Figure 2). The initial spectrum ($t$ = 0 min) displays a weak emission attributed to the small amount of *trans*-stilbene segments originally present in the chain (approximately 370 nm).[13] As further irradiation takes place ($t$ = 2 min), there is an increase in the emission from this band as more of this *trans* isomer is generated; additionally a new emission in the 445–500-nm region appears. After further irradiation, this intense red-shifted luminescence becomes the predominant feature before the polymer precipitates.

A *block* copolymer was prepared by the *sequential* addition of NBE (200 equiv) to a living oligomer of 1 (12 equiv), followed by quenching with benzaldehyde (poly-1 12-*block*-poly($NBE_{200}$); $M_n$ = 20 500, PDI = 1.1). Fluorescence measurements of poly-1 12-*block*-poly($NBE_{200}$)

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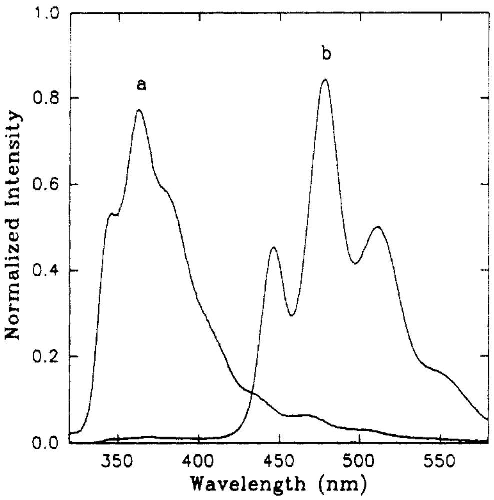

**Figure 3.** Normalized fluorescence spectra ($\lambda_{excitation}$ = 330 nm) of fully irradiated (a) random copolymer of NBE and 1 and (b) poly-1 12-*block*-poly($NBE_{200}$).

are similar to poly-1, but no precipitation is observed even after prolonged irradiation (Figure 3). The addition of a solution containing 10 equiv of 1 and 100 equiv of NBE to 2 yields a *random* copolymer in which the majority of ring-opened 1 is linked to two NBE monomers and occasionally two units of 1 linked in sequence; the possibility of a sequence of three units of 1 is very small. Such a structure is formed because the rate of metathesis of 1 is comparable to that of olefins present in poly(NBE). In this structure the stilbene segments are diluted and not likely to interact with each other. Interestingly, the fluorescence spectrum of this random copolymer is similar to that of *trans*-stilbene (Figure 3).

Results presented above illustrate that paracyclophene derivatives are well-behaved monomers for living ROMP reactions once a careful choice of catalyst is made, in this case one that stereospecifically yields *cis*, and consequently soluble, polymer. The solubility of *cis*-poly-1 relative to *trans*-poly-1 serves to illustrate how kinetic control at the molecular level reflects itself in a product with advantageous bulk properties. Photophysical measurements of poly-1 reveal that its luminescence properties are different from those of solubilized noninteracting stilbene chromophores and are analogous to those observed in systems where the stilbene chromophores interact with each other in a purposely constructed microheterogeneous environment, i.e., aggregates.[14,15] This combination of synthetic flexibility with unusual photophysics should lead to the formulation of novel emissive materials, the preparation of which is interesting in view of their function in the development of photooptical devices.[16] Studies aimed at elucidating both secondary structure effects and the nature of the emittive species are currently being pursued.

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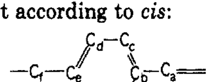
(9) Typical procedure for polymerization of 1: In a nitrogen-filled glovebox a round-bottomed flask was charged with 1 (400 mg, 1.94 mmol) and 2 (15 mg, 0.02 mmol), placed under vacuum, and dry toluene (40 mL) was condensed into it at −78 °C. The resulting clear yellow solution was allowed to warm up to room temperature and stirred an additional 24 h in the dark. Quenching was accomplished by addition of 100 μL of dry benzaldehyde under an argon flow, and the resulting solution was stirred for an additional 1 h. The product was purified by precipitation of a concentrated solution (15 mL) into pentane (250 mL). The resulting cream solid was isolated by centrifugation and placed under vacuum for several hours (yield 350 mg, 87%): $M_n$ = 26 000, PDI = 1.2 (GPC results are calibrated vs polystyrene); $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.24 (d, $J$ = 8 Hz, $C_dH$ or $C_cH$, 4), 6.83 (d, $J$ = 8 Hz, $C_dH$ or $C_cH$, 4), 6.50 (s, $C_aH$, 2), 2.64 (s, $C_fH$, 4); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.5 ($C_e$), 134.9 ($C_b$), 129.6 ($C_a$), 128.7 ($C_c$ or $C_d$), 126.4 (Cc or $C_d$), 37.4 ($C_f$). Assignment according to *cis*:



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