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# Enhanced Photodecarboxylation of an Aryl Ester in Polyethylene Films

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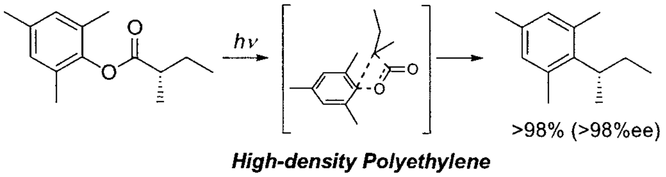
## ABSTRACT



**Photodecarboxylation is the exclusive photoreaction of 2,4,6-trimethylphenyl (*S*)-2-methylbutanoate in unstretched high-density polyethylene films. The sole product, (*S*)-1-(2-methylpropyl)-2,4,6-trimethylbenzene, is formed with complete retention of stereochemistry. In other polyethylene films, organic solvents, and *β*-cyclodextrin cavities, cage-escaped products derived from Fries-type bond scission are obtained as well. The results indicate the importance of the media in controlling the conformations of aryl esters and, thereby, their photoreactions.**

The photochemistry of aryl esters, especially photo-Fries rearrangements, has been studied extensively.[1] In several reports, we have focused on the excited singlet state photodecarboxylations of these compounds,[2] usually a minor pathway, and have investigated ways to increase its importance.[3] In that regard, Finnegan and Knutson[4] have demonstrated that the relative yields of decarboxylation products can be increased markedly when the *o*- and *p*-positions of the aromatic ring are substituted by methyl or other alkyl groups. This methodology has allowed us to study the mechanism of photodecarboxylation of aryl esters in great detail, and we have recently used the stereochemical course of a chiral aryl ester to establish that decarboxylation is a completely concerted process.[5]

Supramolecular photochemistry continues to be exploited, and a large number of interesting hosts or confining media have been described.[6] Among them, zeolites have been exploited extensively because their cationic sites can interact strongly with a guest molecule and their stiff, well-defined cavity walls allow relatively facile interpretations of results from reactions of the guests.[7] Although the diversity of sizes and shapes of cyclodextrin cavities are rather limited, their ease of handling, ready availability, and chirality have led to their extensive use as hosts for photochemical reactions of guest molecules,[8] including cases leading to photochemical asymmetric induction.[9] By contrast, the reaction cavities afforded by polyethylene (PE) films are not as well-defined

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(1) Miranda, M. A.; Galindo, F. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W. M., Lenci, F., Eds.; CRC Press LLC: Boca Raton, FL, 2004; Chapter 42, in press. Miranda, M. A.; Galindo, F. In *Molecular and Supramolecular Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 2003; Vol. 9, pp 43−131 and references therein.

(2) For a review on photodecarboxylation, see: Budac, D.; Wan, P. *J. Photochem. Photobiol. A* **1992**, *67*, 135−166.

(3) (a) Mori, T.; Takamoto, M.; Wada, T. Inoue, Y. *Photochem. Photobiol. Sci.* **2003**, in press. (b) Mori, T.; Wada, T.; Inoue, Y. *Org. Lett.* **2000**, *2*, 3401−3404.

(4) Finnegan, R. A.; Knutson, D. *J. Am. Chem. Soc.* **1967**, *89*, 1970−1972.

(5) Mori, T.; Saito, H.; Inoue, Y. *Chem. Commun.* **2003**, 2302−2303. See also ref 4.

(6) For examples, see: (a) Tung, C.-H.; Wu, L.-Z., Zhang, L.-P.; Chen, B. *Acc. Chem. Res.* **2003**, *36*, 39−47. (b) Weiss, R. G., Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530−536.

(7) (a) Turro, N. J. *Acc. Chem. Res.* **2000**, *33*, 637−646. (b) Scaiano, J. C.; Garcia, H. *Acc. Chem. Res.* **1999**, *32*, 783−793. (c) Ramamurthy, V.; Garcia-Garibay, M. A. *Comput. Supramol. Chem.* **1996**, *7*, 693−719.

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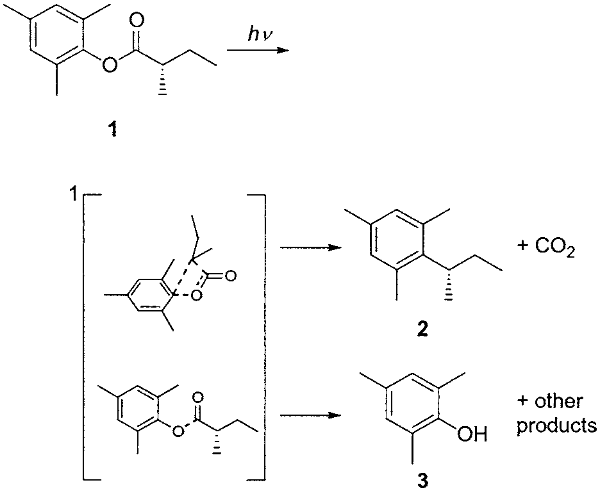
**Scheme 1.** Photoreactions of 2,4,6-Trimethylphenyl (*S*)-(−)-2-Methylbutanoate (1)



in size or shape as those of zeolites or cyclodextrins, and they exist as a distribution. The walls of the PE cavities can exert only passive pressure on guest molecules during their reactions. As a result, the selectivity generally expected of reactions in PE films is less than in zeolites or cyclodextrins.[10]

Here, we report that high reaction selectivity can be achieved during irradiations of (*S*)-1-(2-methylpropyl)-2,4,6-trimethylbenzene (**1**) in polyethylene films and that the course of the reaction can be exclusively decarboxylation (**2**) when the appropriate type of PE film, one of high density, is employed. The results demonstrate that the reaction cavities afforded by PE films can affect the conformations of **1** to enhance the decarboxylation mode and to suppress products from the lysis modes (**3** and products not isolated from the 2-methylbutanoyl radical) (Scheme 1).

Some conformational control of decarboxylation has been already achieved by irradiating 1-naphthyl esters in PE films at varying temperatures.[11] However, even under the most favorable conditions, the major products were from photo-Fries and related radical-rearrangement reactions. Previously, we found that photodecarboxylation of **1** in solutions and under a wide variety of conditions proceeds with complete retention of configuration, indicating that extrusion of $CO_2$ is concerted and involves the spiro-lactonic transition state suggested previously.[4] In these experiments, the phenolic product **3** was always present to an extent that varied with the reaction conditions employed.

Chiral substrates have been employed to investigate the mechanisms of a wide variety of photochemical reactions that are thought to involve radical pair intermediates.[12] For example, we have investigated recently the photoreactions of 1-naphthyl (*R*)-2-phenylpropanoate in PE films to reveal the degree to which PE reaction cavities influence the motions of *pro*-chiral radical pairs.[13] Those radical pair recombinations occur with significant enantiospecificity but significantly less than complete stereospecificity. Thus, a nonconcerted *decarboxylation* of **1** in PE films should not be stereospecific; the observations that they are in PE films supports their concerted nature in these confining media.

In our attempt to improve the yield of the photodecarboxylation product **2** from **1**, we initially investigated the influence of varying the solvent and temperature; however, lysis leading to **3** could not be eliminated.[14] For instance, in methylcyclohexane, temperature dependence of the photoproduct yields indicated the importance of more than one competing process: the relative yield of **2** was 60% at 90 °C and increased as temperature was lowered, reaching the highest value, 87%, at ca. −10 °C and decreasing thereafter (79% at −45 °C). At −80 °C, the rate of photoreaction was too slow to be monitored. Regardless of the reason for this effect, it indicates that modification of temperature alone is unlikely to suppress the processes leading to **3** completely. Thus, we investigated a different strategy, employing PE films as the reaction medium, to improve the relative yields of **2**. The PE films selected[15] represent very different morphologies that are indicated by their percent of crystallinity (given as a suffix to their PE acronyms).[16]

Evidence for the importance of the conformation of **1** on the photochemical course of **1** is provided by DFT calculations for an isolated molecule. The energetically preferred *s-trans* conformation (vide infra) cannot yield **2** unless significant intramolecular motions occur in the excited singlet state. The results in Table 1 indicate that the concentration of the *s-cis* conformation is increased significantly within the ground or excited singlet state of **1** when the ester is placed in the confining reaction cavities afforded by PE films.[5] Furthermore, the importance of reaction cavity shape

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[8] (a) Ueno, A.; Ikeda, H. *Mol. Supramol. Photochem.* **2001**, *8*, 461−503. (b) Bortolus, P.; Monti, S. *Adv. Photochem.* **1996**, *21*, 1−133. (c) Bortolus, P.; Grabner, G.; Koehler, G.; Monti, S. *Coord. Chem. Rev.* **1993**, *125*, 261−268. (d) Ramamurthy, V.; Eaton, D. F. *Acc. Chem. Res.* **1988**, *21*, 300−306.

[9] (a) Sivaguru, J.; Natarajan, A.; Kaanumalle, L. S.; Shailaja, J.; Uppili, S.; Joy, A.; Ramamurthy, V. *Acc. Chem. Res.* **2003**, *36*, 509−521. (b) Turro, N. J. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 4805−4809. (c) Brunet, E. *Chirality* **2002**, *14*, 135−143. (d) Constable, E. C.; Housecroft, C. E. *Chimia* **1999**, *53*, 187−191. (e) Inoue, Y. *Chem. Rev.* **1992**, *92*, 741−770.

[10] (a) Gu, W.; Warrier, M.; Ramamurthy, V.; Weiss, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 9467−9468. (b) Gu, W.; Warrier, M.; Schoon, B.; Ramamurthy, V.; Weiss, R. G. *Langmuir* **2000**, *16*, 6977−6981.

[11] Gu. W.; Abdallah, D. J.; Weiss, R. G. *J. Photochem. Photobiol. A* **2001**, *139*, 79−87.

[12] (a) Gao, F.; Boyles, D.; Sullivan, R.; Compton, R. N. Pagni, R. M. *J. Org. Chem.* **2002**, *67*, 9361−9367. (b) Griesbeck, A. G.; Kramer, W.; Lex, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 577−579. (c) Bhanthumnavin, W.; Bentrude, W. G. *J. Org. Chem.*, **2001**, *66*, 980−990.

[13] Xu, J.; Weiss, R. G. *Org. Lett.* **2003**, *5*, 3077−3080.

[14] Details will be discussed in full paper. See Supporting Information for typical data.

[15] Films employed in this study are an amorphous polymer from DuPont-Dow Elastomers (**PE0**; Nordel IP 3430 containing 42.5 wt % ethylene, 57 wt % propylene, 0.5 wt % ethylidenenorbornene), low-density PE (**PE46**; Sclairfilm SL-1) from DuPont of Canada and linear low-density PE (**PE50**; LL-3001.63) from Exxon Chemical Co., and high-density PE from Polialden Petroquimica, Brazil (**PE68**; type ES-300) or from Exxon Chemical Co. (**PE74**; Exxon HDPE 7745.10). Films were cold-stretched by hand to ca. three (**PE46** and **PE50**) or four (**PE68** and **PE70**) times their original lengths. All films were extracted with chloroform at least three times each before use to remove antioxidants, plasticizers, and other additives, rinsed with fresh hexanes, and dried in vacuo.

[16] By X-ray diffraction with MDI Jade 5 software for X-ray diffraction pattern processing from Materials Data, Inc., Livermore, CA. Also see: (a) Matthews, J. L.; Peiser, H. S.; Richards, R. B. *Acta Crystallogr.* **1949**, *2*, 85−90. (b) Reference 13.

**Table 1.** Photodecarboxylation of 2,4,6-Trimethylphenyl (*S*)-(−)-2-Methylbutanoate **1** in Polyethylene Films[a]

| reaction medium[b] | [**1**] (mmol (kg film)$^{-1}$) | film thickness ($\mu$m) | *T* (°C) | irrad time (min) | conv (%) | product distrib (**2**: **3**) | ee (%) | mass balance (%) |
|---|---|---|---|---|---|---|---|---|
| **PE0**(u) | 2.0 | $1.2 \times 10^3$ | 23 | 60 | 28.0 ± 5.7 | 81.7:18.3 | >98 | 92 |
| **PE46**(u) | 2.7 | 82 | 2 | 90 | 22.6 ± 1.0 | 89.7:10.3 | >98 | 89 |
| | | | 23 | 40 | 12.9 ± 1.3 | 75.5:24.5 | >98 | 93 |
| | | | | 60 | 48.3 ± 9.6 | 71.6:28.4 | >98 | 64 |
| | | | 65 | 20 | 26.3 ± 3.2 | 48.9:51.1 | >98 | 83 |
| **PE46**(s) | 2.7 | 34 | 23 | 40 | 11.2 ± 1.8 | 57.7:42.3 | >98 | 97 |
| | | | | 60 | 30.5 ± 5.4 | 65.1:34.9 | >98 | 78 |
| **PE50**(u) | 5.0 | 25 | 23 | 40 | 14.1 ± 1.6 | 38.2:61.8 | >98 | 87 |
| **PE50**(s) | 5.0 | 16 | 23 | 40 | 28.1 ± 4.9 | 37.1:62.9 | >98 | 74 |
| **PE68**(u) | 19 | 21 | 23 | 60 | 17.4 ± 3.0 | 98.8:01.2 | >98 | 90 |
| **PE68**(s) | 19 | 12 | 23 | 60 | 30.8 ± 4.7 | 82.6:17.4 | >95 | 88 |
| **PE74**(u) | 12 | 17 | 23 | 60 | 18.5 ± 2.3 | 98.8:01.2 | >98 | 88 |
| **PE74**(s) | 12 | 13 | 23 | 60 | 19.9 ± 3.3 | 80.1:19.9 | >98 | 90 |
| $\beta$-CD in $H_2O$ | (0.5 mM) | (1 cm) | 25 | 20[c] | 43 | 64.0:36.0 | (2.0)[d] | 63 |
| methylcyclohexane | (3.1 mM) | (1 cm) | 25 | 5[c] | 15.6 ± 0.4 | 82.1:17.9 | >99[e] | 99 |

[a] Films were immersed in dichloromethane solutions of the ester (ca. 10 mM) for 3 min to 3 h to obtain the desired concentrations, dried, sealed in evacuated quartz cuvettes (unless noted otherwise), and irradiated (low-pressure Hg lamp; ethanol filter; $\lambda = 254$ nm). Photoproducts and remaining **1** were removed by exhaustive extraction and analyzed by HPLC using a DAICEL OJ-H column. See Supporting Information Figure S-3. Each datum is the average of at least three analyses on each of three different films. [b] "u" and "s" refer to unstretched and cold-stretched films, respectively; see text. [c] Quartz filter for irradiations. [d] Racemic ester as substrate. [e] By chiral GC with a SUPELCO $\beta$-DEX 325 column (0.25 $\mu$m; 30 m).

on the reaction course of **1** (and the conformations imposed upon it by the PE films) is demonstrated by the marked *decreases* in the relative yields of the decarboxylation product **2** when the films are stretched. It is known that film stretching causes a net migration of guest molecules such as **1** from reaction cavities in amorphous regions to cavities in the interfacial regions (along the lamellar surfaces of polyethylene crystallites).[17] These results may be compared with those obtained from irradiations in the isotropic solvent, methylcyclohexane, and in aqueous solutions of $\beta$-cyclodextrin,[18] where the relative yields of **2** are less than the optimal ones obtained in PE. However, there is no clear trend between PE crystallinity or other single physical property of the films (see Table S-1 of Supporting Information) and the relative yields of **2**. The natures of the reaction cavities of each film, as well as the effect that they have on the conformations of **1**, must be determined by a combination of the properties. However, the two high density PE films in their unstretched state yield only trace amounts of **3**; *the overwhelming product is* **2**, *and its ee is >98%*. The reaction cavities of the two high-density PE films either force all of the molecules of **1** to adopt *s-cis* conformations, or they prohibit the radical pairs from the alternative reaction pathway leading eventually to **3** to recombine and reform **1**. Whether the decarboxylation pathway is promoted or the escape of radical pairs is attenuated, the result is the same.

In all cases, the material balance is quite high at <30% conversion (where most of the irradiations were analyzed to avoid secondary reactions). In completely amorphous **PE0**, which lacks interfacial sites, the **2**/**3** ratio was quite similar to those obtained in methylcyclohexane solution at a comparable temperature. Given the large differences in the **2**/**3** ratios of **PE46**(u) and **PE50**(u), films of nearly the same crystallinity, perhaps the similarity between the ratios in methylcyclohexane and **PE0** is fortuitous.

As mentioned above, film stretching leads to decreased relative yields of the photodecarboxylation product **2**. Film stretching of partially crystalline PE films redistributes microcrystallites more evenly within the amorphous domains, increases the area of the interfacial region, decreases mean hole free volumes, and increases the fraction of guest molecules in interfacial cavities.[17] Despite these perturbations, the formation of **2** remains stereospecific and, presumably, concerted; a radical mechanism must not be involved, even in the confining reaction cavities of the various unstretched and stretched PE films.

We were unable to obtain reliable fluorescence spectra of **1** in all of the PE films except **PE0** at a high doping concentration, ~50 mmol (kg film)$^{-1}$ (see Supporting Information Figure S-1). The shapes of the absorption and the excitation spectra of **1** are almost the same in methylcyclohexane and PE films, although there appears to be some self-absorption in the former. However, the dynamics of the fluorescence decays ($\lambda_{ex}$ 266 nm; $\lambda_{em}$ 290 nm) in methylcyclohexane (single-exponential decay of 1.6 ns) and **PE0** (two components of 2.9 ns (37%) and 4.8 ns (63%)) suggests that the distributions of conformations for **1** differs in the two media.

DFT calculations of **1** at the B3LYP/6-31(d) level[19] identify four possible conformational minima (See Supporting Information Table S-2). Among them, the two *s-cis* conformers are potential immediate precursors of the spirolactonic transition state required for concerted decarboxy-

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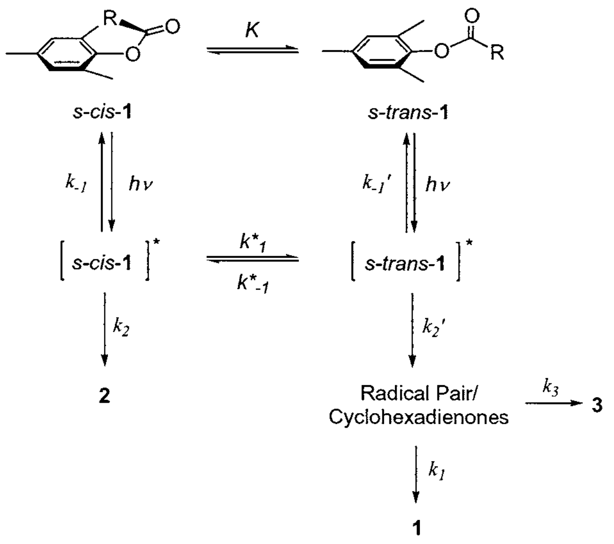
[17] Wang, C.; Xu, J.; Weiss, R. G. *J. Phys. Chem. B* **2003**, *107*, 7015−7025.

[18] Some chiral induction (2.0% ee) was obtained in **2** when racemic ester **1** was irradiated in aqueous $\beta$-cyclodextrin. Details will be presented elsewhere.

**Scheme 2.** Possible Kinetic Steps Involved in *s-cis* and *s-trans* Equilibration and Photodecarboxylation



lation. All of the conformers have significantly larger molecular volumes than the mean free void volumes of the PE films (113−177 Å$^3$),[20] and therefore it seems probable that the reaction cavities do apply severe constraints on the shapes of the guest molecules. Although the calculated "gas phase" distributions predict a ca. 0.1% equilibrium population of *s-cis* conformers, they are more polar than the *s-trans* conformers (See calculated dipole and quadrupole moments in Supporting Information Table S-2) and may be preferred within the somewhat more polarizable interfacial regions.[21]

A possible mechanism involving the interconversion of conformers and the possible photochemical reactions from each (assuming no change of geometries within the short excited-state lifetimes when irradiations are performed in the constraining environments of the PE films) is illustrated in Scheme 2. In low viscosity isotropic solutions, the equilibrium between *s-cis* and *s-trans* conformers in their ground and excited states may affect the **2**/**3** ratio. In **PE0** (and the other PE films), it is reasonable to assume that $k_1^* \ll k_2$ and $k_{-1}^* \ll k_2'$. Assuming the reaction cavities of the high density PE films do not affect the values of $k_{-1}$ and $k_{-1}'$, they may promote formation of the *s-cis* isomer (i.e., larger values of $K$) and faster reversion of the radical pair to starting ester **1** (i.e., increased $k_1/k_3$ ratios).[22] Although both probably contribute to the observed nearly exclusive formation of **2**, we suspect that the major influence is on the value of $K$.

To understand better these processes, the influence of temperature on the irradiation of **1** in **PE46**(u) and in methylcyclohexane has been compared. Within the range 2−65 °C, the changes of ln(**2**/**3**) with respect to the reciprocal of temperature are linear in the polymer, but they are clearly nonlinear in the isotropic paraffin (See Supporting Information Figure S-2). In the latter medium, a linear correlation exists over only a part of the temperature range explored, suggesting that different steps in Scheme 2 may be rate-determining at different temperatures. Additional studies will be required to analyze the specific reasons for the distinctly different temperature dependencies in PE and methylcyclohexane.

In conclusion, photodecarboxylation of the ester **1** can be made the nearly exclusive reaction pathway by performing the irradiations in a high density PE film. The lack of the competitive products from photo-Fries-type lyses can be rationalized on the basis of ground-state conformational control of **1** or by suppression of escape of radical pairs (forcing their recombination and reformation of **1**) by the PE reaction cavities. Ancillary evidence suggests that conformational control is the more important factor, but additional experiments will be required to determine the extent that radical-pair recombinations contribute. The environmentally benign and inexpensive nature of the PE media and the complete retention of chirality in the photodecarboxylated product justify further exploration of the synthetic potential of PE-mediated asymmetric photoreactions.

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**Supporting Information Available:** Schematic presentation of the possible conformations of **1** involved, tables of physical properties of the films employed, DFT calculations of possible conformers, figures of fluorescence spectra of **1** in methylcyclohexane and in **PE0**, the temperature dependence of the **2**/**3** ratio in methylcyclohexane and in **PE46**(u), and typical chiral HPLC chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.

(20) Gu, W.; Hill, A. J.; Wang, X.; Cui, C.; Weiss, R. G. *Macromolecules* **2000**, *33*, 7801−7811.

(21) (a) Lamotte, M.; Joussot-Dubien, J.; Mantione, M. J.; Claverie, P. *Chem. Phys. Lett.* **1974**, *27*, 515−520. (b) Lamotte, M.; Joussot-Dubien, J. *Chem. Phys.* **1973**, *2*, 245−248.

(22) Tung, C.-H.; Yuan, Z.-Y.; Wu, L.-Z.; Weiss, R. G. *J. Org. Chem.* **1999**, *64*, 5156−5161.