Preparation and Ring-Opening Polymerization of 2-*tert*-Butyl-7-oxabicyclo[2.2.1]heptane

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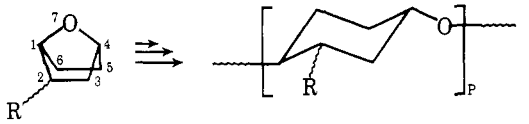
ABSTRACT: New bicyclic ethers, *exo*- and *endo*-2-*tert*-butyl-7-oxabicyclo[2.2.1]heptanes, were prepared and polymerized at temperatures below 0 °C in CH_2Cl_2 with BF_3–THF complex–epichlorohydrin system. Polymerizations of either monomer ceased at low conversions when the temperature was −20 °C or lower. Stereochemistry of the polymerizations was studied by NMR analysis of the product polymers. The configurations of the 1,2,4-trisubstituted cyclohexane ring in the polymers from exo and endo monomers were cis,trans (*a,e,a*) and trans,trans (*e,e,e*), respectively. Rapid termination was suggested by infrared detection of end groups in the polymer.

This paper describes the synthesis and polymerization of 2-*tert*-butyl-7-oxabicyclo[2.2.1]heptane. Before the present study, 7-oxabicyclo[2.2.1]heptane (**1a**), a bicyclic ether monomer, was polymerized to a high melting polymer, in which the cyclohexane unit was assumed to give a 1,4-trans configuration.[1] Polymerizations of *exo*- (**1b**) and *endo*-2-methyl-7-oxabicyclo[2.2.1]heptanes (**1c**) have also been studied.[1–4] In addition, Kops and Spanggaard prepared two isomers of 2,6-dimethyl-7-oxabicyclo[2.2.1]heptane, and polymerized them with PF_5 initiator.[5]



1a, R = H
b, R = *exo*-CH_3
c, R = *endo*-CH_3
d, R = *exo*-$(CH_3)_3C$
e, R = *endo*-$(CH_3)_3C$

Stereochemical and kinetic studies of polymerizations of **1b** and **1c** were reported by us.[6–8] S_N2 propagation between the monomer and the propagating bicyclic oxonium ion was established. The influence of the methyl substituent on the reactivity was discussed with respect to the geometric exo and endo positions. In the present study, *exo*- and *endo*-2-*tert*-butyl-7-oxabicyclo[2.2.1]heptanes, **1d** and **1e**, were employed. In general, the *tert*-butyl group gives a more pronounced effect in respect to steric hindrance.

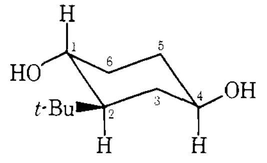
Preparation of 1d and 1e

Hydrogenation of *tert*-butylhydroquinone with Raney Ni catalyst in MeOH at 150–160 °C under H_2 pressure of 96 kg/cm^2 gave a mixture of steric isomers of 2-*tert*-butylcyclohexane-1,4-diols containing significant amounts of a ketonic compound (a characteristic ir band at 1706 cm^{-1}). The mixture was then treated with $NaBH_4$ until the band at 1706 cm^{-1} disappeared. It was heated with activated alumina at 250–260 °C under nitrogen to give a mixture of several reaction products (by VPC) which contained **1d** and **1e** in a ratio of about 5:1. Pure **1d** and less pure **1e** were isolated from reaction mixture by distillation using a spinning band column. Further purification of **1e**, containing small amounts of **1d** and some other impurities, was achieved by means of preparative gas chromatography on Carbowax 6000. These monomers were identified by elemental analysis, NMR and ir spectra as described in the Experimental Section. Distinction between two isomers of **1d** and **1e** was made as follows. According to Allinger's rule,[9] the endo isomer should have a higher boiling point than the exo isomer. **1e** boiled at 10 °C higher temperature than **1d**. In NMR spectroscopy, it is assumed according to the McConnel's equation[10] that some ring hydrogens, especially at endo position, of **1e** may be shielded by the *tert*-butyl group in the endo position. Therefore, the hydrogens of **1e** are to be located at higher field. In fact, the ring hydrogens of **1e** showed the highest resonance peak at δ 0.8 ppm, whereas those of **1d** at δ 1.1 ppm. Additionally, the *tert*-butyl group of **1e** showed a singlet peak at about 0.1 ppm lower field than that of **1d.**

Stereochemistry of Propagation of Polymerizations of 1d and 1e

Polymerizations of both **1d** and **1e** were carried out in CH_2Cl_2 with BF_3-tetrahydrofuran (THF) complex–epichlorohydrin (ECH) system under nitrogen at −20 °C. Polymers were isolated by evaporation of solvent and unreacted monomer, and were purified by reprecipitation in methanol-water to give viscous oily materials. Molecular weights of poly **1d** and poly **1e** were 480 and 660, respectively, by VPO. The NMR spectra of poly **1e** and poly **1d** are shown in Figures 1a and 1c.

In Figure 1a, two broad peaks centered at δ 1.2 and 2.0 are assignable respectively to axial and equatorial hydrogens of the cyclohexane ring of poly **1e.** This assignment is based on the fact that the signal of axial hydrogen of methylcyclohexane appears at about 0.5 ppm higher field than that of the corresponding equatorial hydrogen.[11] The broad band at δ 2.8–3.8 is assigned to two axial methyne hydrogens of the C-1 and C-4, since, as described in our paper,[6] the axial methyne hydrogens adjacent to hydroxy groups in 4-*tert*-butylcyclohexanol[12] and 2-*tert*-butyl-4-hydroxycyclohexanol[13] give peaks of larger half-width at higher field than the corresponding equatorial hydrogens. The big signal at δ 0.96 and the minor peak at δ 3.62 are due to *tert*-butyl group and poly(ECH), respectively. Other small downfield peaks could not be accurately assigned. Presumably, these peaks are due to the polymer end groups formed in termination reactions as discussed below. This spectrum is very similar to that of a model compound, *trans*-2-*tert*-butyl-*trans*-4-hydroxycyclohexanol (**2**), which was isolated by preparative gas chromatography from the hydrogenation product of *tert*-butylhydroquinone (Figure 1b). In the spectrum of **2** in CD_3OD (**2** is insoluble in $CDCl_3$), very broad bands at δ 1.0–1.7 and δ 1.7–2.2 are apparently assignable to the axial and equatorial ring hydrogens, respectively. Bands at δ 2.8–4.1 are assigned to axial C-1 and C-4



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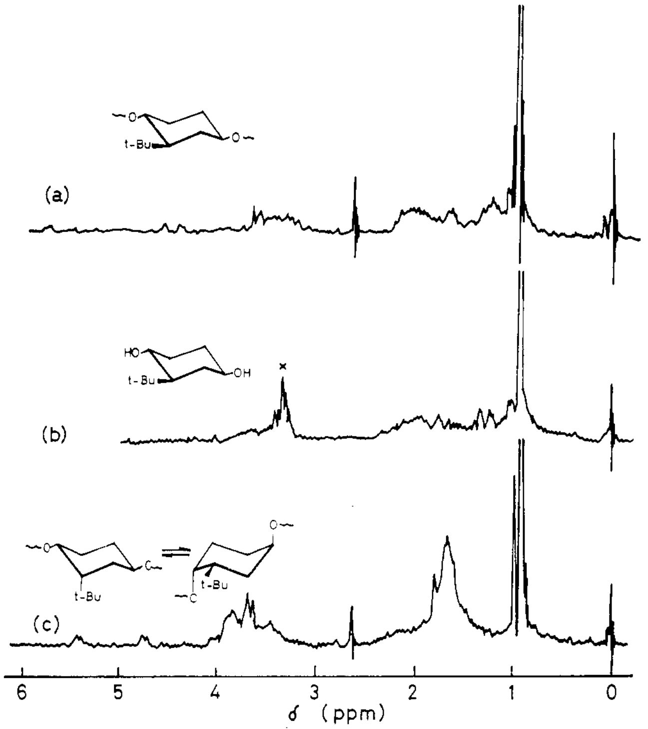


Figure 1. NMR spectra of (a) poly **1e**, (b) *trans*-2-*tert*-butyl-*trans*-4-hydroxycyclohexanol (**2**), and (c) poly **1d**: (a) and (c), $CDCl_3$, 100 MHz; (b) CD_3OD, 60 MHz; x, proton due to undeuterated methanol.

methyne hydrogens, which show characteristic large widths.

Based on these observations, it is concluded that the 1,2,4-trisubstituted cyclohexane ring of poly **1e** has the same configuration (trans,trans structure) as that of the model compound **2**, i.e., three substituents of the ring are at equatorial positions. The structure of poly **1e** is formed by nucleophilic backside attack of **1e** onto the C-4 carbon of the propagating oxonium ion (**3e**) to cause the Walden inversion of configuration of the C-4 carbon (Scheme I, where A^- is a counteranion etc.).

On the other hand, the NMR spectrum of poly **1d** (Figure 1c) is quite different from that of poly **1e**, i.e., the band due to the cyclohexane ring has a complicated multiplet centered at δ 1.6 and two α-methyne hydrogens at lower fields of δ 3.44 and 3.84 in comparison with the corresponding hydrogens of poly **1e**. This spectrum seems to indicate the presence of a conformational equilibrium, such as poly **1d** $\rightleftharpoons$ poly **1d′**, which is produced by the SN2 reaction between the oxonium **3d** at C-4 and the monomer **1d** (Scheme I). The conformer poly **1d′** is predominant (favorable free energy) due to the equatorial *tert*-butyl group, and the methyne hydrogens at C-1 and C-4 take mainly equatorial positions. The attack of monomer at C-1 of **3d** is not considered to be the main course of propagation on the basis of NMR analysis of **1d**.

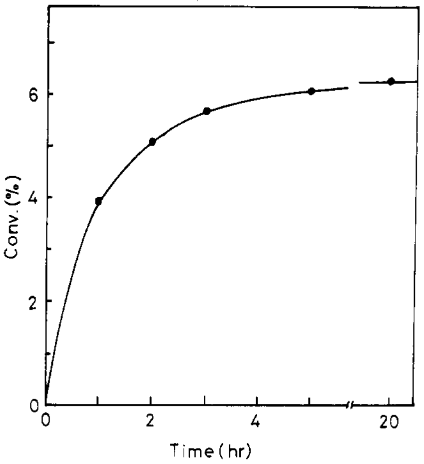


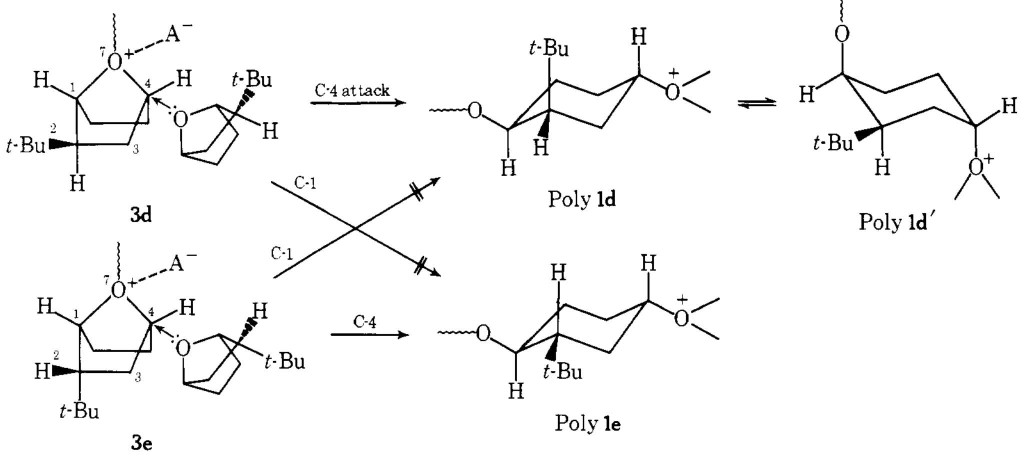
Figure 2. Time–conversion curve of polymerization of **1d** in CH_2Cl_2 solution at −15 °C: $[M]_0 = 2.25$; $[BF_3\text{–}THF]_0 = 4.13 \times 10^{-2}$; $[ECH]_0 = 3.08 \times 10^{-2}$ mol/l.

Termination in Polymerization of 1d and 1e

A mechanism of termination in the polymerization of 7-oxabicyclo[2.2.1]heptanes has been studied by some investigators.[1-3] Baccaredda et al. examined the termination reaction in the polymerization of **1b** by quantitative analysis for fluorine in the polymer and uv spectroscopy. In the polymerization of **1d** in the present study, termination reaction occurred at a considerable rate as indicated by the time–conversion profile (Figure 2).

In Figure 3 are shown ir spectra of the **1d** polymers obtained under various conditions. When the polymerization at −30 °C was short stopped by sodium phenoxide after 45 min (the phenoxyl end-capping method[14]), the ir spectrum of the obtained polymer shows absorption bands due to phenoxyl group at 1604, 1587, 1497, 801, 751, and 698 cm^{-1} in addition to bands characteristic of the polyether (Figure 3a). The ir spectra of the polymers obtained at 0 °C after

Scheme I



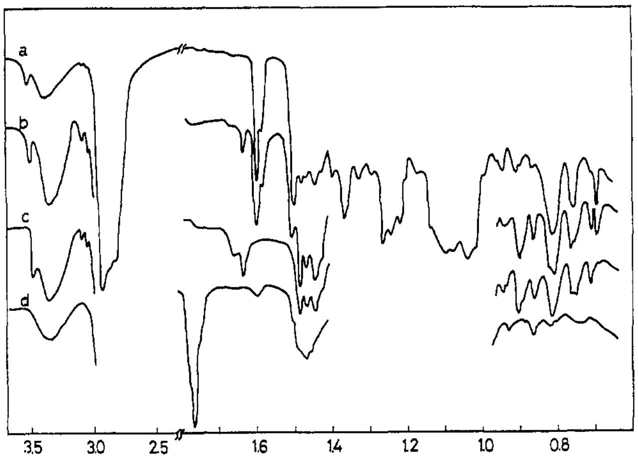
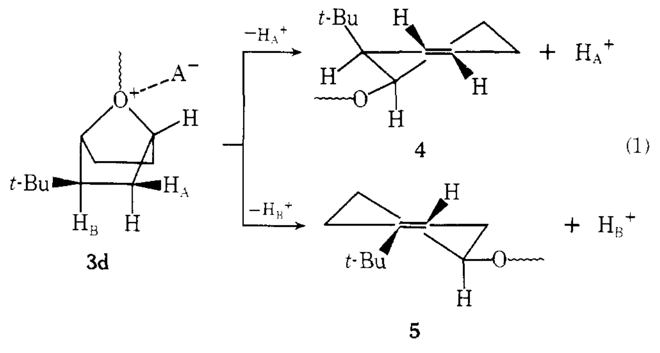


Figure 3. Ir spectra of polymers of **1d**: (a) polymer obtained at −30 °C after 45 min; (b) at 0 °C after 30 min; (c) at −10 °C after 240 min; (d) polymer after hydroboration of poly **1d**.

30 min and at −10 °C after 240 min show new absorption bands at 3090, 3050, 1664, 1638, 885, 841, 748, and 697 cm^{-1} (Figure 3b and 3c), and the spectrum 3c does not have the bands due to the phenoxyl group. The absorption bands at 1664, 748, and 697 cm^{-1} may be assigned to cis-disubstituted olefin (**4**), and those at 1638, 885, and 841 cm^{-1} to trisubstituted olefin (**5**).[15] In the assignment of the latter, frequency at 1638 cm^{-1} due to $\nu_{C=C}$ is lower than the usual value of 1670 cm^{-1}. Justification of this assignment is found in the fact that $\nu_{C=C}$ appears at 1645 cm^{-1} in 4-*tert*-butylcyclohex-3-enol.[16] A product obtained by hydroboration of the poly **1d** (obtained at 0 °C after 30 min) followed by refluxing in propionic acid gave an ir spectrum (Figure 3d) in which all of the above olefinic bands disappeared completely and a strong band due to propionate ester appeared at 1750 cm^{-1}. In the NMR spectrum of poly **1d** (Figure 1c), minor peaks at δ 4.8 and δ 5.4 may be assigned to olefinic protons.

These facts are taken to indicate that the poly **1d** prepared at higher temperature containes an olefinic linkage at the polymer end. The following scheme may explain the termination with formation of olefinic linkage at the polymer end.



Figures 4a and 4b show ir spectra of two samples of poly **1e** under different conditions. In the case of **1e** also, the formation of olefinic linkage in the termination step is indicated by the absorption bands at 3050, 1672, 810, 742, and 707 cm^{-1}, characteristic of a cis-disubstituted olefin. Elimination of the hydrogen (H_a, H_b or H_c) in the strained oxonium ions, which are suffering from increased steric repulsion due to the *tert*-butyl group, would release the strain.

The above terminations become significant with a decrease in the monomer concentration and with an increase of the reaction temperature. In polymerizations of methyl analogoues at conversions below 10%, no production of the olefinic ends could be detected. In addition, it is suggested that the proton eliminated from the oxonium ions in eq 1 and 2 cannot participate in reinitiation of the present polymerization system, since the consumption of monomer ceased completely at very low conversions (Figure 2), and the phenoxyl group was not introduced into the product polymer by the phenoxyl end capping when the polymerization was carried out at higher temperatures, e.g., −15 °C.

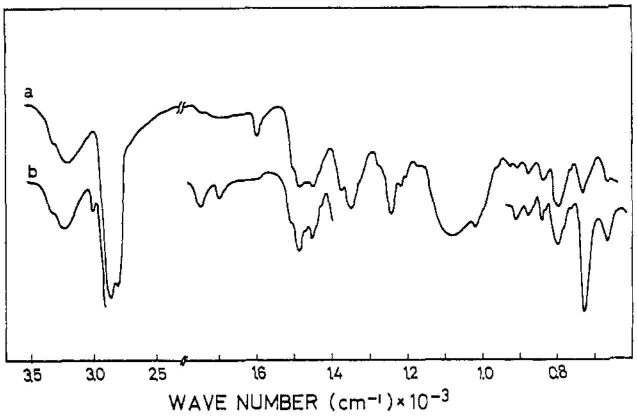
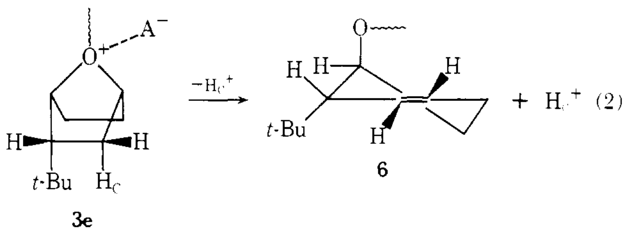


Figure 4. Ir spectra of polymers of **1e**: (a) polymer obtained at −20 °C after 40 min; (b) at 0 °C after 50 min.



Experimental Section

Materials. *exo*- and *endo*-2-*tert*-Butyl-7-oxabicyclo[2.2.1]heptanes (1d) and (1e). Commercial *tert*-butylhydroquinone (100 g) was hydrogenated over W-2 Raney Ni catalyst (6 g) in MeOH (100 ml) at 150–160 °C and 96 kg/cm^2. The reaction mixture was freed of catalyst, and the MeOH solution was treated with $NaBH_4$ (9 g) at 20–30 °C until the ir absorption band at 1706 cm^{-1} disappeared completely. The solution was then evaporated in vacuo after addition of a small amount of acetic acid. The residue was distilled at 155–162 °C (12 mm) to give a viscous pale yellow material. The isomeric mixture (100 g) of 2-*tert*-butyl-1,4-cyclohexanediols was treated with 130 g of activated alumina (preheated at 500–600 °C for 4 h) under nitrogen. The mixture was heated gradually to 260 °C and kept at 250–260 °C for 10 h. Volatile fractions were distilled out under reduced pressure (60–70 mm) at intervals of 2 h. The distillate was collected and extracted with ether, separated from the aqueous layer, and dried over anhydrous K_2CO_3. The ether solution was evaporated to give a residue (50 g) boiling at 70–150 °C. The crude product was fractionated using a 100-cm column equipped with spinning band. The fractions distilled at 192.0–192.5 °C and 193–204 °C were pure **1d** (purity >99.9% and overall 21% yield based on *tert*-butylhydroquinone) and less pure **1e** (contaminated with **1d** and some impurities as shown by gas chromatography), respectively. Redistillation of the higher fraction yielded a fraction of bp 202–203 °C (purity > 96.0% and 4% yield). Final purification of **1e** was successfully achieved by preparative gas chromatography employing an 1.5 m × 7 mm column packed with 15% carbowax 6000 on celite (60–80 mesh) at 90 °C with hydrogen (0.6 kg/cm^2) as carrier gas. These monomers were identified on the basis of their elemetal analyses, NMR, and ir data. **1d**, NMR ($CDCl_3$) δ 0.87 (s, 9 H), 1.1–2.0 (m, 7 H), 4.45 (m, 2 H); ir (liquid film) 1009, 948 cm^{-1}. Anal. Found: C, 78.16; H, 11.96. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. **1e**, NMR ($CDCl_3$) δ

0.97 (s), 0.8–2.5 (m), 4.48 (m); ir (liquid film) 1012, 949 cm^{-1}. Anal. Found: C, 78.05; H, 11.84.

***trans*-2-*tert*-Butyl-*trans*-4-hydroxycyclohexanol (2).** The above diol was isolated from an isomeric mixture of the hydrogenation product by preparative gas chromatography using a 3.0 m × 3 mm column packed with carbowax 6000 on 60/80 celite at 178 °C with hydrogen gas (1.0 kg/cm^2). Crude diol obtained was recrystallized from acetone to yield a product with mp 174–175 °C (sealed tube). The structure of 2 has been established by the following results. The melting point is different from the melting points of the two known isomers, i.e., *cis*-2-*tert*-butyl-*cis*-4-hydroxycyclohexanol,[17] mp 152.5–153.5 °C, and *trans*-2-*tert*-butyl-*cis*-4-hydroxycyclohexanol,[13] mp 156.5–157.7 °C. The NMR spectrum of the diacetylated sample of 2 in CCl_4 showed a broad peak due to two methyne hydrogens at C-1 and C-4. It is generally known that the NMR peak of the axial methyne hydrogen is broad, whereas that of the equatorial one is sharp.[13,14] Thus, the two methyne hydrogens of 2 are reasonably assumed to be at the axial positions. The elemental analysis of 2 is in agreement with the calculated values. Found: C, 70.01; H, 11.84. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Its NMR spectrum is shown in Figure 1b.

Polymerization Procedure. BF_3–THF complex (catalyst), ECH (promotor), and CH_2Cl_2 (solvent) were purified as previously described.[6–8] Polymerization was carried out under dry nitrogen and stopped by the addition of Na phenoxide in THF. The polymer solution in CH_2Cl_2 was washed with aqueous NaOH, dried over anhydrous K_2CO_3, and finally evaporated to dryness in vacuo. Further purification of the polymer was performed by methanol (solvent)–water (precipitant) reprecipitation.

Hydroboration of Poly 1d. To 90 mg of poly 1d in diglyme (2 ml) was added $NaBH_4$ (15 mg) at 0 °C and then BF_3–etherate (0.03 ml) after stirring for 2 hr. The suspension was kept overnight at room temperature and refluxed in propionic acid (1 ml) for 4 h. The reaction mixture was diluted with water, extracted with ether, and washed with aqueous $NaHCO_3$. The ether solution was evaporated to dryness in vacuo.

Measurement of NMR and Ir. Nuclear magnetic resonance spectra were determined in $CDCl_3$ or CD_3OD on a PS-100 or C-60H (Jeol Ltd.) at room temperature. Infrared spectra were recorded on a DS-301 spectrometer (Nihon Bunko Co., Ltd) as film coated on a NaCl plate.

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Kinetics of Delayed Luminescence and Triplet Energy Migration in Poly(*N*-vinylcarbazole)

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ABSTRACT: The kinetics of phosphorescence and delayed fluorescence of solid films of poly(*N*-vinylcarbazole) have been examined over a temperature range from −150 to −75 °C. Delayed fluorescence intensities (I_{df}) go through a maximum at −100 °C, but phosphorescence intensities (I_p) decrease monotonically with increasing temperature. At −100 °C and with sufficiently low light intensities I_{df} and I_p are biphotonic and monophotonic, respectively. Both luminescence intensities decay exponentially at −100 °C and the lifetimes show an approximate factor of 2 ratio as expected for annihilation delayed fluorescence. A better explanation for the lifetime data is provided if one assumes that the delayed fluorescence arises from an annihilation process involving a mobile triplet and an immobile triplet excimer. In any case, it appears that triplet migration is intermolecular in character.

Triplet energy migration in polymers has been studied by a number of techniques involving phosphorescence or delayed fluorescence measurements.[1–8] Most of the earlier work was carried out on frozen solutions, but more recently, solid polymer films have been studied as well. Of special interest in the present work is the study of Cozzens and Fox,[5] who demonstrated that frozen solutions of poly(1-vinylnaphthalene) display an intramolecular type of triplet energy transfer judging from the kinetics of the delayed fluorescence emission and the behavior of triplet quenchers.

Because of our recent interest in the mobility of triplets in liquid solutions of monomeric species, as measured by spatially nonhomogeneous irradiation,[9] it was decided to study the kinetics of polymer delayed luminescence to see if conditions could be found such that this same experimental technique could be applied to polymer systems. The major question to be settled was whether or not annihilation (or P type) delayed fluorescence ever occurs by a mechanism involving intermolecular triplet migration. The question is important since the technique of spatially intermittent radiation cannot be applied when the triplet–triplet processes are intramolecular in character. Obviously, dilute frozen solutions are a poor choice for study and so it was decided to examine the kinetics of phosphorescence and delayed fluorescence of solid polymer films.

At the commencement of this work, no published reports of delayed fluorescence from a solid polymer film could be found. In recent months, however, Fox and co-workers[7] have reported on studies of delayed fluorescence from solid films of poly(vinylnaphthalene) and its copolymers with methyl methacrylate and with 2-naphthyl methacrylate as