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Co-Polymerization of Maleimides and Vinyl Ethers: A Structural Study

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ABSTRACT: We report on the thermally-induced and photoinduced polymerization of the electron-donating divinyl ether di(4-vinyloxybutyl)succinate (DVBS) and the electron accepting 1,5-bis(maleimido)-2-methylpentane (BMMP) and their monofunctional analogues, dodecylvinyl ether (DDVE), *N*-methylmaleimide (NMM), and *N*-phenylmaleimide (NPM). We focus on the stoichiometry of the monomer constituents consumed in the polymerization and the structural identity and bonding configuration(s) of the polymer products. For both BMMP−DVBS and NMM−DDVE, FTIR and ^{1}H NMR data indicate 1:1 stoichiometry for the resulting polymer. For both systems, the polymers are of the alternating donor and acceptor form $(DA)_n$. This result holds for both photoinduced and thermally induced reactions. Structural NMR studies of polymers synthesized from both mono- and difunctional monomers indicate the presence of both *cis* and *trans* conformers of the acceptor at the D−A bond. This finding indicates that thermodynamic factors alone are not sufficient to explain the ratio of the conformers and either steric factors or features specific to the transition state play a significant role in determining the conformational distribution of the polymer.

Introduction

Photopolymerization is one of the most rapidly expanding processes for materials production. Photopolymerizations have gained prominence in recent years for the pollution-free curing of polymer films as well as emerging applications in dental materials, conformal coatings, electronic and optical materials, and high resolution rapid prototyping of 3D objects. These solvent-free polymerizations proceed very rapidly with a fraction of the energy requirements of thermally cured systems, and the resulting polymers possess useful material properties. For example, these reactions can be used to form highly cross-linked, thermally stable polymer films exhibiting excellent adhesion, abrasion resistance, and chemical resistance while not emitting or requiring volatile organic components. In addition to the broad utility of such polymers, the photopolymerization process itself affords advantages such as very high reaction rates at room temperature and spatial control of polymerization.

To date, most of the work on UV-initiated photopolymerizations has focused on free-radical systems based primarily upon acrylate and methacrylate monomers.[1−3] The kinetics of these free-radical photopolymerizations and the structural properties of the resulting polymers have been characterized extensively. Acrylate monomers polymerize rapidly and are modified at the ester functionality, allowing access to materials with a variety of properties. These systems are, however, not without their limitations. Monomeric acrylates are relatively volatile, have an unpleasant odor, and present potential safety hazards. Oligomeric acrylates are much less volatile, but are highly viscous, making processing a significant challenge. The free radical photopolymerization reactions undergone by acrylates are inhibited by oxygen, and if high polymerization rates are required, the reactions must be carried out under an inert atmosphere. Finally, these polymerizations require the presence of a photoinitiator, which places limits on the long-term stability of the monomer formulation and leaves undesired residues in the final polymer product.

Photopolymerizations mediated by electron donor−acceptor interactions have emerged relatively recently as a new process[4−7] and they are not yet understood fully. While there is a body of literature concerned with these polymerization reactions,[12−23] there remain significant ambiguities relating to mechanism and kinetics of formation. The work we present here focuses on the characterization of the products formed by photopolymerization of the donor divinyl ether molecule di(4-vinyloxybutyl)succinate (DVBS) and the acceptor 1,5-bis(maleimido)-2-methylpentane (BMMP) without use of an initiator additive. Because cross-linking is extensive in this system (vide infra), we have used the monofunctional monomers dodecylvinyl ether (DDVE) and *N*-methylmaleimde (NMM) for comparison to produce linear (un-cross-linked) chains. In addition, for purposes of NMR structural resolution, we have also used the monomer *N*-phenylmaleimide (NPM) with DDVE in the formation of non-cross-linked copolymers. The structures of these monomers are presented in Figure 1. The two points we consider in this paper are the stoichiometry of the monomer constituents in the photoinduced polymerization and the structural identity of the polymer formed by both photoinduced and thermally induced reactions. Our data indicate that the polymer is of the form $(DA)_n$. FTIR and ^{1}H NMR data indicate 1:1 stoichiometry for polymer formation with both the photoinduced and thermally induced reactions. ^{1}H and ^{13}C NMR data on the monofunctional monomers DDVE, NPM, and NMM, and the corresponding linear polymers, allow the assignment of bands in the spectra

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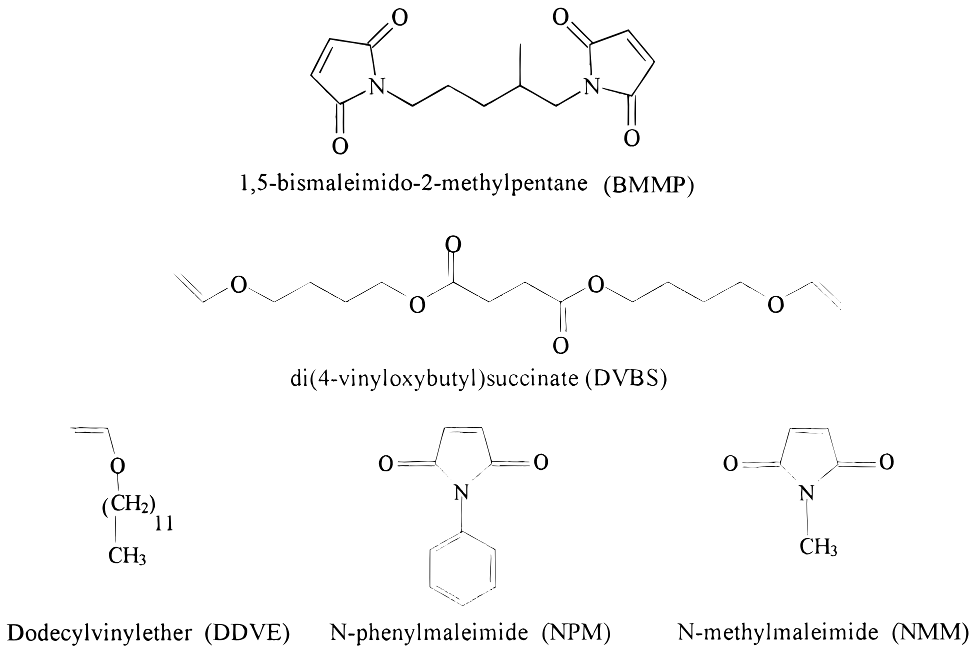

1,5-bismaleimido-2-methylpentane (BMMP)

di(4-vinyloxybutyl)succinate (DVBS)

Dodecylvinylether (DDVE) N-phenylmaleimide (NPM) N-methylmaleimide (NMM)

Figure 1. Chemical structures of the monomers used in this work.

of the polymer synthesized from the difunctional monomers BMMP and DVBS. The data on the BMMP−DVBS copolymer indicate that the bonding of the monomer units exhibits approximately equal amounts of *cis* and *trans* conformers across the unsaturation of the maleimide monomer. Simple thermodynamic considerations are not sufficient to explain this ratio of conformers because they differ in energy by ~2.3 kcal/mol, and therefore either steric factors or the identity of the transition state act to mediate the conformational distribution seen in the polymer product. This is the first report in a series aimed at understanding the molecular processes at work in photopolymerizations mediated by electron donor−acceptor interactions. Following the structural characterization presented here, we will examine the formation kinetics and reaction dynamics of these systems using transient spectroscopic techniques.[8]

Experimental Section

NMR Spectroscopy. ^{1}H NMR spectra were recorded at 300 MHz on Varian Inova-300, Gemini-2000 and Varian VXR-300 spectrometers and at 500 MHz on a Varian VXR-500 spectrometer. The proton-decoupled ^{13}C NMR spectra were recorded on Varian Inova-300, Gemini-2000, and Varian VXR-300 spectrometers at 75.46 MHz and at 125.75 MHz on a Varian VXR-500 spectrometer. The solid-state CP/MAS ^{13}C spectra were recorded at 100.58 MHz on a Varian VXR-400 spectrometer with samples spinning at a speed of either 4.0 or 5.4 kHz. For monomer ^{1}H NMR spectra, 64 scans were usually taken while ^{13}C NMR spectra required, typically, 2048 scans to achieve a useful signal-to-noise ratio. For polymers, ^{1}H and ^{13}C NMR spectra required 25 000−50 000 scans to achieve a useful signal-to-noise ratio.

FTIR Spectroscopy. The FTIR spectra (4000−700 cm^{-1}) were obtained using a Nicolet Magna-IR 550 spectrometer equipped with a N_2(l)-cooled MCT-A detector. For kinetic studies, one or two drops of a mixture of BMMP and DVBS monomers were spread uniformly over a gold-coated substrate, and the sample was mounted in a grazing incidence external-reflectance accessory. At least 256 scans were taken at 4 cm^{-1} resolution to achieve an adequate signal-to-noise ratio.

Molecular Weight Measurements. The molecular weights of copolymers were determined using a Beckman GPC model 100A with a Waters R401 differential refractometer detector.

Thermal Analysis. Glass transition temperatures, T_g, were determined under N_2 atmosphere using a Perkin-Elmer DSC 7 and a heating rate of 20 °C/min. The thermogravimetric analysis was carried out under N_2 atmosphere on a Perkin-Elmer TGA 7 with 10 °C/min heating rate.

Chemicals. Maleic anhydride (ARCO Organic), 2-methyl-1,5-diaminopentane, acetic anhydride, methanol, and *N*-methylmaleimide (Aldrich), benzene (J. T. Baker), and triethylamine (Spectrum Chemical Mfg. Corp.) were used as received. Chloroform-*d* (99.8% with 1% v/v TMS) and DMSO-d_6 (99.9% purity) were purchased from Cambridge Isotope Laboratories. Di(4-vinyloxybutyl)succinate (DVBS) by Allied Signal and dodecylvinyl ether (DDVE) was donated by International Specialty Products, and both compounds were used as received.

Preparation of 1,5-Bis(maleimido)-2-methylpentane (BMMP). BMMP was prepared in two steps,[9] with minor modifications as noted below. The first step in the synthesis of BMMP is the preparation of 2-methylpentane-1,5-bis(maleic acid) (MPBMA). Maleic anhydride (2 mol) in benzene (200 mL) was stirred while being maintained between 40 and 45 °C. 2-Methyl-1,5-diaminopentane (1 mol) was added dropwise over a period of 1 h. The resulting suspension was stirred for an additional hour. A white crystalline precipitate was collected by suction filtration and washed with hexanes and water to yield 2-methylpentane-1,5-(bismaleic acid) (typical yield 92%): mp 131−132 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.83 (d, 3 H of CH_3), 1.10 (m, 1 H), 1.3−1.6 (m, 6 H of CH_2), 3.0−3.15 (m, 4 H of CH_2 adjacent to two NH), 6.2−6.4 (m, 4 H of C=C), 9.1 (q, 2 H of COOH). IR (cm^{-1}): 3262, 3123, 3084, 2956, 2877, 1706, 1641, 1531, 1410, 1302, 853, 796.

The second step is the preparation of BMMP from MPBMA. 2-Methylpentane-1,5-(bismaleic acid) (0.1 mol), triethylamine (0.4 mol), and acetone (100 mL) were added to a single flask. The solution was refluxed and acetic anhydride (0.3 mol) was added dropwise. The solution was cooled to room temperature after refluxing for 24 h. The resulting dark brown solution was added to 200 mL of icecold water. After 2 h of stirring, a dark brown precipitate was obtained by suction filtration and dried in air. The crude product was purified using a packed silica gel column eluted with 40% ethyl acetate/60% hexane. The purified product was recrystallized from 50% aqueous methanol to yield white crystals of BMMP (typical yield 28%): mp 87−89 °C. ^{1}H NMR (300 MHz, $CHCl_3$-*d*): δ 0.83 (d, 3 H of CH_3), 1.10 (m, 1 H), 1.3−1.6 (m, 6 H of CH_2), 3.35−3.5 (m, 4 H of CH_2 adjacent to N of two imide rings), 6.66 (d, 4 H of C=C of two imide rings). ^{13}C NMR ($CHCl_3$-*d*, 75.46 MHz): δ 17.3, 25.8, 31.2, 32.2, 37.8, 43.7,134.9, 134.0, 170.7,

171. IR (cm^{-1}): 3452, 3166, 3092, 2969, 2935, 1767, 1699, 1612, 1584, 1410, 1446, 836. Absorption $\lambda_{max} = 300$ nm. Fluorescence $\lambda_{max} = 460$ nm.

BMMP−DVBS Copolymer Synthesis. All copolymers were synthesized without the addition of a photoinitiator. BMMP and DVBS were heated to 40 °C in the absence of solvent to make a homogeneous solution. The flask containing this solution was maintained at 40 °C and flushed with dry nitrogen for 10 min and then sealed. Photoexcitation was done with either a N_2 laser (337 nm) or by a mercury lamp source (UV output 4.5 mW/cm^2). When the N_2 laser was used, only BMMP molecules were excited because 337 nm lies in the tail of the BMMP absorption spectrum. Photoexcitation of both constituents is possible when the broadband mercury light source is used. For either excitation scheme, a nominally white product with a slight yellow tint was obtained. The product was washed sequentially with hot chloroform, hexanes, methanol, and water and dried overnight in vacuo at room temperature. The product was insoluble in methanol, chloroform, acetone, hexane, and cyclohexane.

For the thermally induced reactions, monomers were heated to 60 °C in $CHCl_3$ for 24 h under N_2. The solvent was evaporated and the product redissolved in a minimum amount of acetone followed by precipitation from methanol.

*Copolymer Synthesis of N-*Methylmaleimide/Dodecylvinyl Ether. In a typical reaction, *N*-methylmaleimide (NMM) and dodecylvinyl ether (DDVE) were added to a round-bottom flask with a small amount of $CHCl_3$ solvent. The $CHCl_3$ solvent was required because NMM is not soluble in DDVE. The rest of the polymerization was the same as reported above. The reaction yielded a slightly yellow-white polymer which was purified by precipitation from methanol after dissolving in acetone. The molecular weight of the polymer, determined by GPC was $M_n = 35\,000$.

Results and Discussion

The purpose of this paper is to provide the foundation for further studies on donor−acceptor-mediated photopolymerization using transient spectroscopic techniques. The key points in understanding maleimide−vinyl ether systems are determination of the reactivity of the monomers with themselves and the stoichiometry of the copolymer. It is also important, of course, to understand the chemical structure and extent of cross-linking in the final polymer product. We present data relevant to each of these points in the sections that follow.

Our first step in understanding this system was to determine whether the individual monomers would homopolymerize in the presence of either light or heat. BMMP, NPM, NMM, DVBS, and DDVE each yielded no detectable homopolymer under the conditions used to polymerize mixtures of BMMP and DVBS, NMM and DDVE, or NPM and DDVE.

Stoichiometry of the Monomers. We have used FTIR and ^1H NMR spectroscopy to study the polymerization of BMMP and DVBS. From the chemical structures in Figure 1, it is clear that there can be several possible structures for the photopolymer product, with the extent of cross-linking being the dominant variable. Before evaluating the cross-linking, however, we must first understand the intermolecular bonding arrangement that is responsible for the polymerization in the first place. Since there are several possible bonding schemes which may appear plausible, it is not necessarily clear that a 1:1 stoichiometry will hold or that an alternating (D−A) repeat unit is appropriate. We consider the FTIR and NMR data separately.

Infrared Data. In the BMMP−DBVS mixed monomer system, two different reactive functionalities are present, i.e. the unsaturations in the imide ring of the acceptor (BMMP) and vinyl unsaturations at the termini of the donor (DVBS). To characterize the kinetic behavior of the system completely, both reactive sites need to be monitored separately. Our FTIR data shown in parts a and b of Figure 2 are the spectra of BMMP and DVBS in the 1500−1800 and 2800−3200 cm^{-1} regions, respectively. The BMMP C═C stretching resonances at 1612 and 1584 cm^{-1} are highly overlapped with the intense C═C stretching resonances of DVBS at 1618 and 1638 cm^{-1} (Figure 2a). The C═O resonances, while not overlapped for the two monomers, do not provide any kinetic information because these functionalities are not consumed in the reaction. We use these bands as internal standards. We note that it is difficult to define a baseline for these spectra due to the multiple strong absorptions in this region. For these reasons, even though the C═C bonds are the reactive functionalities, it is not easily possible to monitor the progress of the polymerization in the 1500−1800 cm^{-1} spectral region. The alkene CH stretching bands between 3100 and 3200 cm^{-1} were chosen for monitoring the kinetic behavior of the copolymerization (Figure 2b) because spectral overlap and baseline assignment problems are less serious for these resonances. The 3092 cm^{-1} band of BMMP and the 3118 cm^{-1} band of DVBS were selected because of their relatively high absorptivity, and while they are overlapped, we have been able to define a baseline for each of these bands.

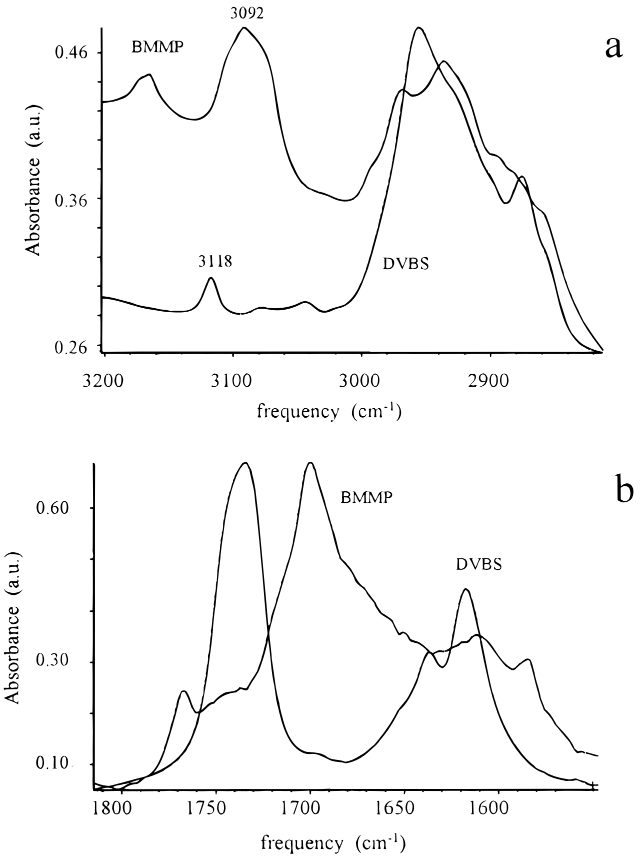

Figure 2. IR spectra of BMMP and DVBS monomers. (a) 2800−3200 cm^{-1} and (b) 1500−1800 cm^{-1}.

In a typical experiment, BMMP and DVBS are added to a gold-coated quartz substrate, and the spectrum of the reaction mixture is recorded before photopolymerization and at selected exposure times. These data are curve fit after baseline correction.[10] To ensure the uniqueness and reproducibility of the results, the Gauss-

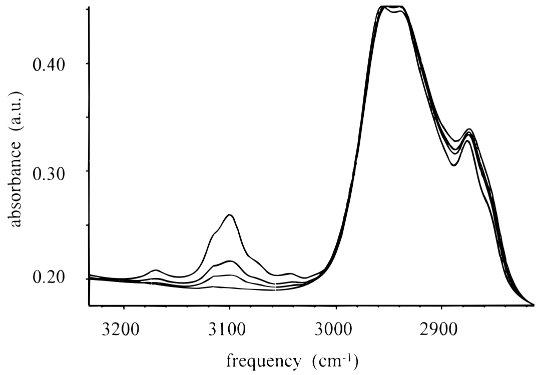

Figure 3. Variation of band intensities for the monomer alkene CH stretching resonances during photocopolymerization of BMMP/DVBS. Times for each spectrum are $t = 0$ min, $t = 30$ min, $t = 53$ min, and $t = 12$ h, in order of decreasing intensity of the ~3100 cm^{-1} bands.

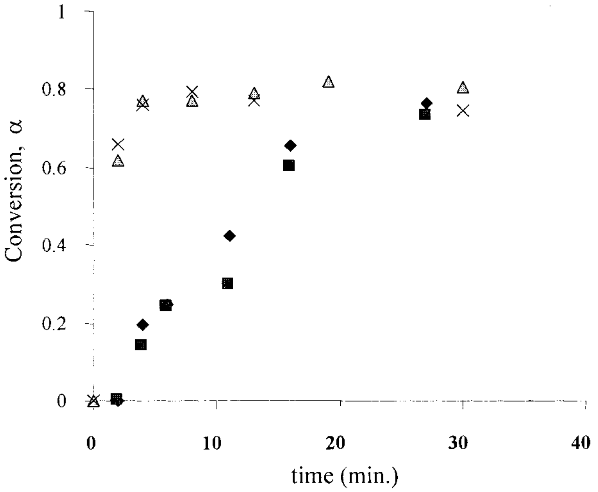

Figure 4. Time-dependence of polymerization of monomers for photoinduced and thermally induced reactions with initial 1:1 BMMP to DVBS monomer stoichiometry at $T = 22$ °C. Key: ◆ = BMMP conversion, thermally induced reaction; ■ = DVBS conversion, thermally induced reaction; ▲ = BMMP conversion, photoinduced reaction; × = DVBS conversion, photoinduced reaction.

ian peak width, the number and position of the peaks, and the baseline are fixed and the peak heights are varied to optimize the fit.

The fractional conversion of the BMMP and DVBS unsaturations is an indication of degree of copolymerization and is defined as[11]

$$\alpha = 1 - \frac{A_t}{A_0} \qquad (1)$$

where A_0 and A_t represent absorbances at times zero and t, respectively. From Beer's law, the monomer concentrations C_0 and C_t obtain directly. The change in the intensity of the alkene CH stretching vibrations is shown as a function of time in Figure 3. These spectra are normalized for C=O stretching resonance intensity. The alkene CH stretching resonance decreases monotonically with UV exposure time. This progression shows that the double bonds of both the BMMP acceptor and DVBS donor have reacted (Figure 4), but their relative rates of reaction are of importance in establishing the stoichiometry of the product. The conversion vs time data for BMMP and DVBS are shown in Figure 5 for initial monomer ratios of $[BMMP]_0/[DVBS]_0 = 1$ (Figure 5a) and appearance of the alkene CH resonances reflects a 1:1 reaction stoichiometry.

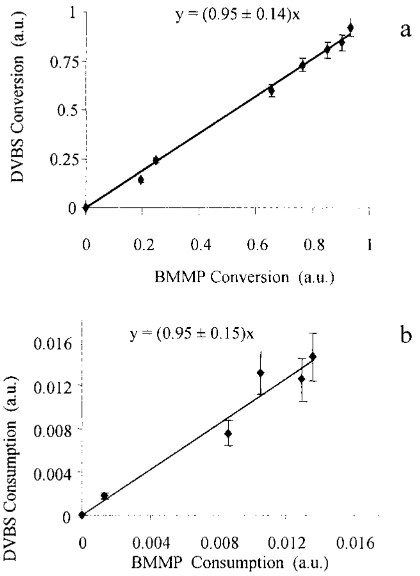

Figure 5. FTIR measurement of BMMP monomer loss vs. DVBS monomer loss in the thermally induced reaction for (a) $[BMMP]_0/[DVBS]_0 = 1$ at T = 22 °C and (b) $[BMMP]_0/[DVBS]_0$ $^1/_2$ at T = 22 °C.

The copolymerization proceeds with UV excitation at room temperature without the use of a photoinitiator. The initial rate of reaction is high and is dependent on the incident UV photon flux. For our conditions, within minutes of initial irradiation, more than 60% conversion of the monomers is seen and after this initially high rate, the reaction slows considerably. A total of 150 min at the same irradiation intensity is required to achieve 80% conversion of the unsaturations, although the approach to this conversion is slow and mostly completed within 15 min.

Despite the rapid photoinduced reaction, we must also consider the possibility that the copolymerization can proceed in the absence of light. We show in Figure 4 the comparison of conversion of monomers as a function of time in the presence and absence of UV irradiation. The thermally induced conversion curve is offset by 2 min because the first FTIR spectrum was collected 2 min after initial mixing (22 °C) as the polymerization proceeds, both monomers disappear at the same rate (Figure 5) for a variety of initial monomer feed ratios.

In an effort to verify the 1:1 stoichiometry of the reaction as established by FTIR measurements and also determine if there is a temperature dependence to the reaction, we have investigated the polymerization reaction of relatively dilute solutions of monomers using ^1H NMR measurements. The data were recorded over a range of reaction conversions from 0% to 5% at 30 °C in DMSO-d_6. For these experiments, the initial mole ratios of the monomers were varied between 1:2 and 2:1. For all reactions, the disappearance of monomer resonances at the reactive functionalities occurred with a 1:1 stoichiometry over the completion range monitored (Figure 6). At 90 °C, the reaction was also observed to proceed with 1:1 stoichiometry. These data support the results obtained with FTIR measurements and demonstrate that the polymerization reaction between BMMP and DVBS proceeds with 1:1 stoichiometry.

Because we have established earlier that homopolymerization of the monomers does not proceed measur-

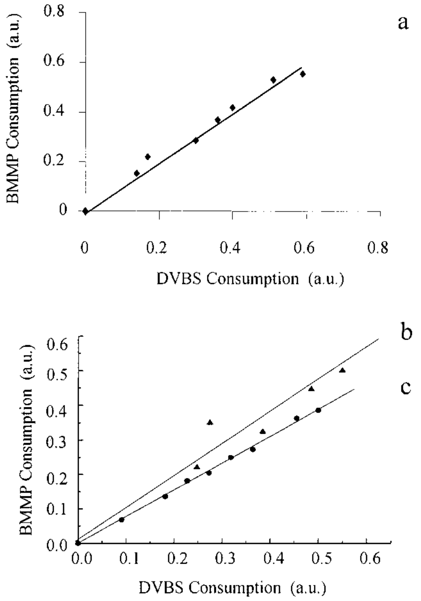

Figure 6. ^{1}H NMR determination of BMMP monomer loss vs DVBS monomer loss. For all data, total conversion = 5%. (a) $[BMMP]_0/[DVBS]_0 = 0.19$ M/0.38 M = $^1/_2$, $T = 30$ °C, slope = 1.0 ± 0.01; (b) ▲ = $[BMMP]_0/[DVBS]_0 = 0.19$ M/0.63 M = 3/1, $T = 90$ °C, slope = 0.93 ± 0.09; (c) • = $[BMMP]_0/[DVBS]_0 = 0.53$ M/1.00 M = 1/1.89, $T = 90$ °C, slope = 0.78 ± 0.08.

ably, we conclude that the copolymer must be alternate in nature, i.e. $-(DVBS-BMMP)_n-$. This finding is in agreement with other literature reports on similar chemical systems.[12−17] While the UV-induced polymerization rate is very fast in the first 2 min and achieves close to a limiting conversion after 5 min, the thermally induced reaction is significantly slower. Within 30 min the conversion in both cases has achieved the same value (~80%) This limiting conversion is in good agreement with that reported by Martuscelli et al.[11] for polymerizations of bis(maleimide) with unsaturated polyester resins. This limiting value is reasonable for highly cross-linked systems and can be understood in the context of trapping of reactive moieties in the rigid polymer matrix. Polymerization of NMM and DDVE, where extensive cross-linking is precluded, achieves greater than 90% conversion.

We next turn our attention to the structural possibilities that exist for this system consistent with the stoichiometric and reaction constraints that we have established above. The $(BMMP-DVBS)_n$ copolymer is insoluble in many solvents, consistent with the expected extensive cross-linking in the product. The key point to understanding the fundamentals of the polymerization reaction is to determine the conformation of the bonding arrangement between the donor and acceptor functionalities. Specifically, the orientation of the succinimide protons will be determined by the mechanism of the reaction.[12−14,26] If the reaction is concerted, which one could expect based on the formation of the complex, the *cis* conformer is expected. Conversely, if the reaction is sequential, such that the reaction across the imido unsaturation proceeds in a stepwise fashion, we would expect the presence of both *cis* and *trans* conformers. In the simplest case, the relative abundance of *cis* and *trans* conformers will be given by the relative thermodynamic stability of the *cis* and *trans* conformers. We have synthesized polymers from NPM and DDVE monomers for this study because the resulting polymer is more soluble than the BMMP−DVBS polymer and

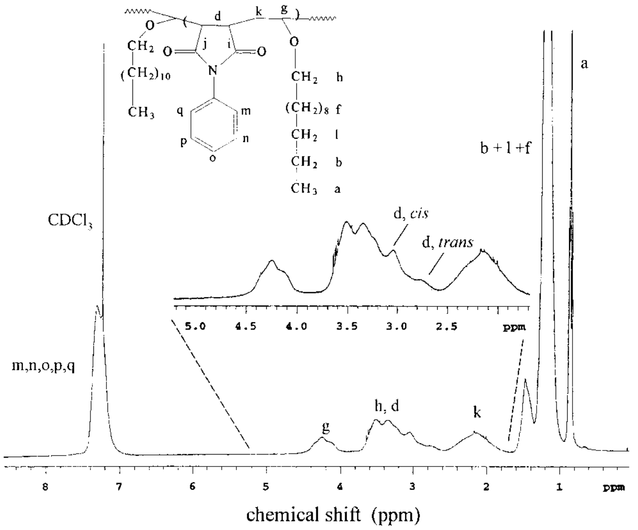

Figure 7. ^{1}H NMR spectrum of photoinduced NPM/DDVE copolymer in $CDCl_3$. Band assignments are indicated according to the inset structure.

the bonding configuration is expected to be the same as that for BMMP−DVBS. The solubility of $(NMM-DDVE)_n$ allows the use of higher resolution, solution phase NMR measurements to elucidate the bonding configuration between the monomer units.

The ^{1}H NMR spectrum of the NPM−DDVE polymer is presented in Figure 7. The NMR peak assignments and proton integrations indicate that the $(NPM-DDVE)_n$ stoichiometry is 1:1, in correspondence with the $(BMMP-DVBS)_n$ polymer. ^{1}H and ^{13}C NMR spectroscopy of $(NPM-DDVE)_n$ can give information about the stereochemistry of the copolymers formed and thus about the propagation mechanism.

Figure 7 shows the ^{1}H NMR spectrum of photoinduced copolymer obtained in high yield (>90%). The lines are very broad because of high molecular weight of the copolymer ($M_n = 14\,310$). The resonances in the 2.7−3.8 ppm region are associated with the methylene protons adjacent to oxygen of vinyl ether and the succinimide protons. These protons are of primary interest in determining the dominant polymerization mechanism. We have also measured and assigned the ^{13}C NMR spectra of NPM−DDVE (Figure 8) and NMM−DDVE (not shown) and summarize our assignments in Table 1.

The NPM−DDVE copolymer possesses three chiral centers, two in the succinimide ring and one at the methine carbon of the vinyl ether. These centers can exist as different diastereomers with different chemical shifts in both ^{1}H and ^{13}C NMR spectra. We present in Table 2 the chemical shifts of selected compounds that have been used to compare to the chemical shifts of NPM−DDVE and NMM−DDVE, and thereby gain stereochemical information about the succinimide moiety. The *cis* succinimide/succinic anhydride proton resonances appear downfield relative to those for the *trans* conformer. Careful examination of the broad ^{1}H resonances between 2.6 and 3.8 ppm for NPM−DDVE (Figure 7) reveals four distinguishable features. We assign the features at 3.05 and 2.7 ppm to the succinimide ring *cis* and *trans* conformers, respectively. The *cis* peak area appears to be larger than that for the *trans* conformer. This is, of course, only a qualitative assessment because of the extensive band overlap present in this region. The NMM−DDVE ^{1}H NMR spectrum (not

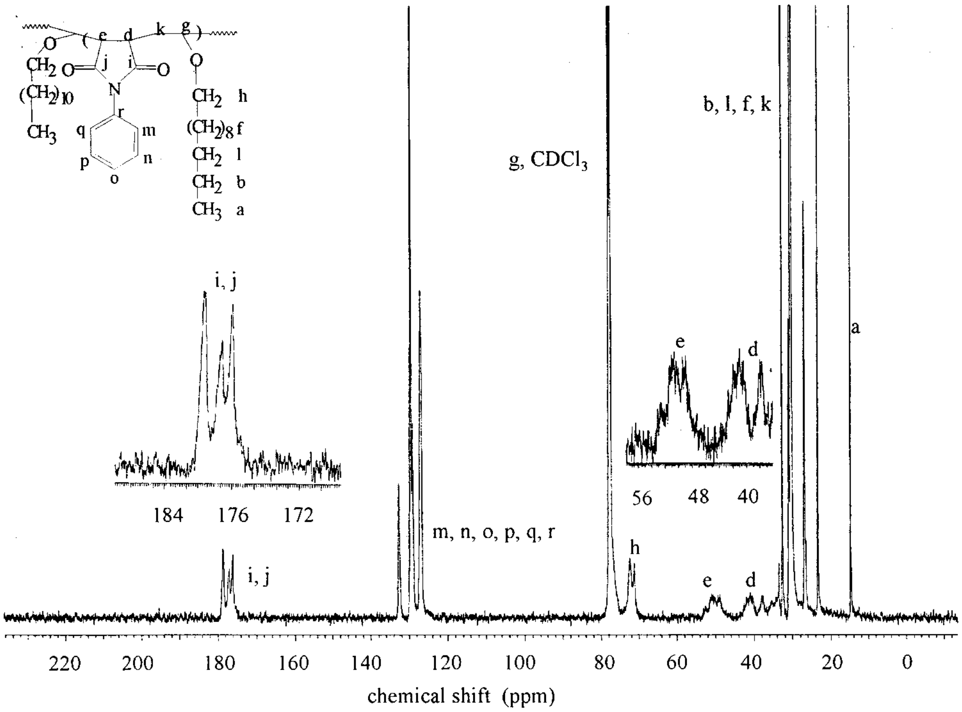

Figure 8. ^{13}C NMR spectrum of photoinduced NPM/DDVE copolymer system in $CDCl_3$. Band assignments are indicated according to the inset structure.

Table 1. ^{1}H and ^{13}C Chemical Shift Assignments for NPM−DDVE and NMM−DDVE

atom	succinimide chem shift (ppm)	
	^{1}H	^{13}C
a (DDVE methyl)	0.85	14
b, l, f, k (methylene)	0.9−2.4 (very broad)	32−20
c (methyl of NMM)	2.9 (broad)	27
e (methine of succinimide)	3.2 (*cis*) and 2.7 (*trans*) (NPM−DDVE) unresolved (NMM−DDVE)	38 and 42 (NPM−DDVE) 37 and 41 (NMM−DDVE)
d (methine of succinimide)	3.2 (*cis*) and 2.7 (*trans*) (NPM−DDVE) unresolved (NMM−DDVE)	48−54 (broad) (NPM−DDVE) 45−53 (broad) (NMM−DDVE)
h (methylene adjacent to oxygen)	3.3−3.7 (broad)	61 and 63(both)
g (methine adjacent to oxygen)	4.0−4.4 (broad)	74−77 (under $CDCl_3$triplet)
m, n, o, p, q	7.0−7.5 (broad)	127,129,130,133
i, j (carbonyl groups)	...	175−179 (NPM−DDVE) 175−180 (NMM−DDVE)

Table 2. ^{1}H and ^{13}C Chemical Shifts of Various Model Compounds at the Succinimide/Succinic-acid/Anhydride

model compound	succinimide/succinic acid/anhydride chem shift (ppm)	
	^{1}H	^{13}C
meso-2,3,-dimethylsuccinic acid (in $CDCl_3$)[29]	2.54	42.05
rac-2,3,-dimethylsuccinic acid acid (in $CDCl_3$)[29]	2.65	41.03
cis-3,4-dimethyl-*N*-phenylsuccinimde (in DMSO-d_6)[12]	...	37.99
trans-3,4-dimethyl-*N*-phenylsuccinimde (in DMSO-d_6)[12]	...	42.42
cis-hexahydro-*N*-phenylphthalimide (in $CDCl_3$)[12]	...	40.06
trans-hexahydro-*N*-phenylphthalimide (in $CDCl_3$)[12]	...	47.52
cis-1,2-cyclohexanedicarboxylic anhydride (in $CDCl_3$)	3.36,[28] 3.2 [27]	45,[28] 39.83[27]
trans-1,2-cyclohexanedicarboxylic anhydride (in $CDCl_3$)	2.95,[28] 2.85 [27]	47,[28] 45.60[27]
maleic anhydride-tetrahydrofuran copolymer[29]	3.3, 3.5	46.6, 49.1
model compound maleic anhydride−tetrahydrofuran 1:1 adduct[30]	3.3	44.2
cis-2,3-dimethyl-*N*-ethylsuccinimde[31]	2.95	...
trans-2,3-dimethyl-*N*-ethylsuccinimde[31]	2.41	...
maleic anhydride-methyl vinyl ether copolymer[32]	...	51.6−48.4, 41.1−37.8
2-propenylisocynate−maleic anhhydride copolymer[26]	3.82 (cis) and 3.68 (trans)	57, 59 and 62, 64

shown) does not reveal this same information because the succinimide proton resonances are obscured by those of the *N*-methyl group. The ^{13}C spectra of the NPM−DDVE copolymer shows distinct peaks from succinimide carbon from *cis* and *trans* configurations. These data are shown in Figure 8. The succinimide carbon-*e* resonances between 48 and 54 ppm show two unresolved peaks that are consistent with *cis* and *trans* conformers. Similarly, carbon-*d* also shows two moderately resolved peaks at 39 and 41 ppm. Unfortunately, the resolution of these resonances is not sufficiently high to allow their quantitation. It is clear, however, that both carbon-*d* and carbon-*e* in the copolymer exist as both *cis* and *trans* conformers.

As noted above, in addition to the copolymerization of maleimides and vinyl ethers by photoinduction,

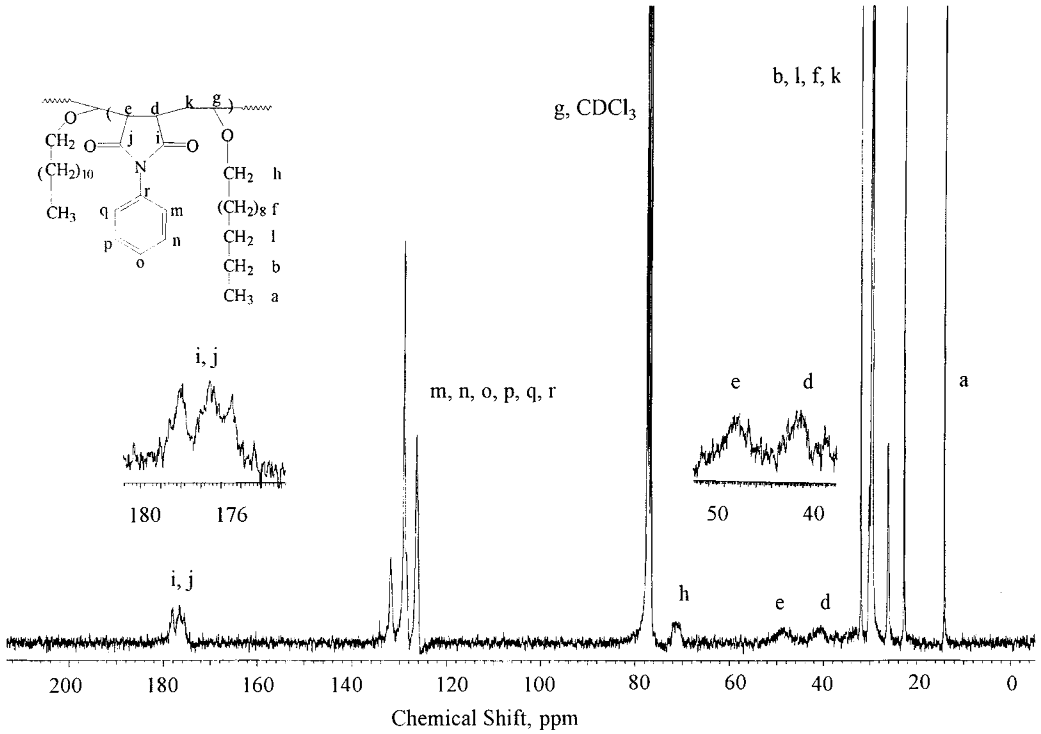

Figure 9. ^{13}C NMR spectrum of thermally induced NPM/DDVE copolymer in $CDCl_3$. Band assignments are indicated according to the inset structure.

thermally induced copolymerization is also significant. It is important to determine whether the copolymer formed by the thermal pathway is the same as that formed by photoinduction. This information could bear directly on the initial step in the polymerization reaction of this system and explain in part the stereochemical data we have determined from the NMR measurements. The ^{13}C NMR spectrum of thermally induced NPM−DDVE is shown in Figure 9. This spectrum is essentially identical to that shown in Figure 8 for photoinitiated NPM−DDVE.

After understanding the stereochemical information on the non-cross-linked copolymer, we are now in a position to interpret the solid-state CP/MAS spectrum of the photoinduced BMMP−DVBS copolymer. The low resolution spectrum presented in Figure 10a shows the solid-state CP/MAS spectrum of the photoinduced BMMP−DBVS copolymer. The resonances are broad and featureless, but the chemical shifts of different bands are consistent with those of the NPM−DDVE and NMM−DDVE copolymers. Specifically, we can assign the broad shoulder between 19 and 22 ppm to the methyl carbon-*a* of BMMP and methylene carbons-*d* of DVBS. The strong resonance centered at ∼ 32 ppm is due to methylene carbons-*h* and -*i* from the BMMP and DVBS monomers. The succinimide carbons-*f* and -*f′* do not reveal any splitting because of the limited spectral resolution.

The NMR data are useful, if only qualitatively, to evaluate the stereochemistry of the polymerization and thereby infer the mechanism. Although unambiguous stereochemical information on the BMMP−DVBS cross-linked copolymer cannot be obtained from the CP/MAS measurements, the presence of significant amounts of both conformers is clear and points to the fact that the polymerization reaction is not concerted, despite the implication of a DA complex as the propagating unit (vide supra).

Recently, Hoyle et al.[4] reported on a maleimide−acrylate copolymerization, and their findings are applicable to the interpretation of our data. Maleimide radicals can initiate the alternating copolymerization in which maleimide acts both as photoinitiator as well as comonomer. Using ^{1}H NMR spectroscopy, Mormann and Schmalz showed that protons on substituted succinic anhydride exhibit more *cis* than *trans* conformers.[26] Our semiempirical calculations indicate that the *trans* conformer of *N*-methyl(2,3-dimethyl)maleimide is more stable than the *cis* conformer by 2.3 kcal/mol.

If the mechanism of D−A bond formation involves an intermediate state that bridges the maleimide unsaturation, then the dominant conformer will be *cis*. If the bond formation is mediated either by radical formation or H abstraction, then we expect that there will be a statistical distribution of conformers with their relative populations being related to the thermodynamic stability of the two conformers. The fact that we observe what appears to be more *cis* than *trans* conformer in the final polymer can be attributed to one of several possibilities. The first is that both mechanisms are operative and the relative contribution of a cyclobutane-like intermediate to produce *cis* conformer (side-on attack of the maleimide unsaturation) compensates for the thermodynamic advantage of the *trans* conformer in the radical-mediated reaction. A second possibility is that the transition state for the reaction is not related in an intuitive manner to either of the final conformers but is such that the probability of forming the two possible conformers is approximately equal. We note that a steric argument would seem to favor *trans* over *cis*, and it is thus unlikely that steric hindrance mediates the reaction.

As noted above, we recover substantially the same result for the thermally induced copolymerization as for the photoinitiated reaction. This finding would argue that radical initiation by H abstraction from a photo-

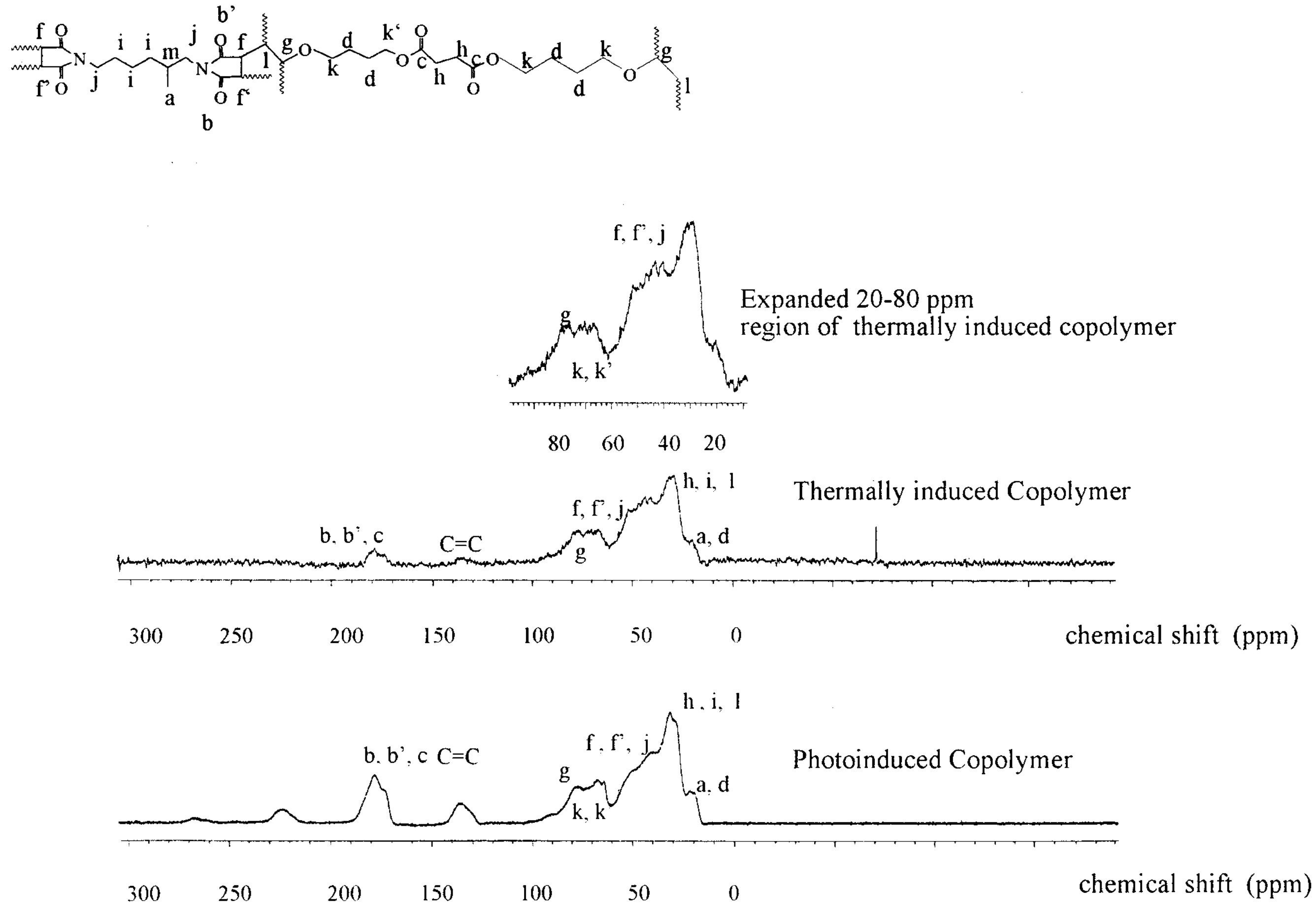

Figure 10. CP/MAS spectra of BMMP/DVBS copolymer. Key: bottom, photoinduced BMMP/DVBS copolymer; center, thermally induced copolymer; top 0−90 ppm expanded region of thermal copolymer spectrum.

Table 3. Physical and Thermal Properties of Various Maleimide/Vinyl Ether Copolymers

copolymer	M_n	T_g (°C)	T_i[a] (°C)	T_f[b] (°C)
BMMP−DVBS (photoinduced copolymer)	NA	NA	320	680
BMMP−DVBS ("dark" copolymer)	NA	NA	250	<800
NPM−DDVE (photoinduced copolymer)	14310	96	345	430
NPM−DDVE ("dark" copolymer)	54054	95	370	430
NMM−DDVE	35000	83	350	420
BMMP−CVE[d]	NA[c]	NA	380	<800
BMMP−DDVE	NA	NA	350	<505

[a] T_i is the temperature at which 10% weight is lost. [b] T_f is the temperature at which 90% weight is lost. [c] NA: not applicable. [d] 1,5-bis(maleimido)-2-methylpentane/cyclohexylvinyl ether copolymer.

excited triplet state is the initial and most important step in the reaction to determine the conformational distribution of the final copolymer.

Thermal and Physical Properties of Copolymers. The thermal properties of bismaleimide/divinyl ether copolymers has been reported on before,[19,20] and we present our data in an effort to allow comparison to earlier work in this area. Table 3 shows different physical and thermal properties of different maleimide−vinyl ether copolymer systems. Both the photoinduced and thermal-induced NPM−DDVE copolymers show roughly the same T_g. We are interested in understanding the role of cross-linking in determining the physical properties of the polymers. We expect that the extensive cross-linking characteristic of BMMP−DVBS will give rise to thermal degradation properties that are superior to those for the corresponding non-cross-linked polymer. We show in Figure 11 and Table 3 the thermogravimetric analysis (TGA) data for BMMP−DVBS and NMM−DDVE. The data demonstrate that the BMMP−DVBS cross-linked polymer exhibits greater thermal stability than the NMM−DDVE system, as expected.

Conclusion

We have investigated the polymerization of the bifunctional monomers BMMP and DVBS and their monofunctional counterparts, NMM, NPM, and DDVE. On the basis of FTIR and NMR data, we conclude that the polymerization of both systems proceeds with 1:1 stoichiometry. The structural ^{1}H and ^{13}C NMR data indicate that neither the photoinduced nor the thermally induced polymerization produces stereospecific products. Rather, the maleimide monomer copolymerizes with vinyl ethers to yield both *cis* and *trans* conformers across its unsaturation. The formation of the same polymer structure by both means of initiation suggests strongly that a radical mediated initiation step is rate limiting. With this fundamental structural information in hand, the next step in characterization of these polymer systems is to understand the kinetics

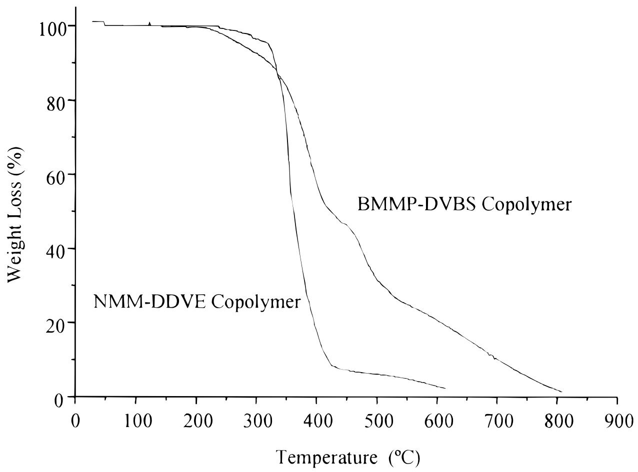

Figure 11. TGA curves for NMM/DDVE and BMMP/DVBS copolymers.

and mechanism of the actual polymerization event. We are in the process of developing this understanding using time-resolved spectroscopies to monitor the motional and population dynamics of the maleimide moieties during polymerization. Making the connection between dynamical data and the extent of cross-linking could provide insight into controlling the molecular processes that give rise to the bulk properties of the formed polymer.

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