Effects of Solvent Basicity on Free Radical Polymerizations of N,N′-bismaleimide-4,4′-diphenylmethane Initiated by Barbituric Acid

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ABSTRACT: The polymerizations of N,N′-bismaleimide-4,4′-diphenylmethane (BMI) initiated by barbituric acid (BTA) carried out in a variety of solvents at 130°C were studied. The nitrogen-containing cyclic solvents such as N-methyl-2-pyrrolidinone acted as a catalyst to promote the formation of the three-dimensional crosslinked network structure. By contrast, the polymerization in a cyclic solvent that did not contain nitrogen such as γ-butyrolactone resulted in nil gel content. The higher the solvent basicity, the larger the amount of insoluble polymer species formed. The molar ratio of BTA to BMI also played an important role in the polymerizations. The resultant polymers, presumably having a hyper-branched structure, exhibited much narrower molecular weight distributions than those prepared by conventional free radical polymerizations. The BMI polymerizations using BTA as the initiator could not be adequately described by conventional free radical polymerization mechanisms. A polymerization mechanism that took into account the generation of a ketone radical pair between BTA and BMI and the subsequent initiation, propagation and termination reactions was proposed. It was concluded that the nitrogen-containing cyclic solvents were capable of participating in the ketone radical pair formation process, thereby increasing the extent of polymer crosslinking reactions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 596–603, 2010

Key words: bismaleimide polymerization; barbituric acid initiation; ketone radical pair; solvent basicity

INTRODUCTION

Bismaleimide-based thermoplastic and high performance thermosetting resins are widely used in industry due to their desirable cost/property advatages.[1–3] Bismaleimide monomer consists of a backbone of imide structure and two terminal reactive groups (—C═C—), which can undergo polymerization.[4,5] Difunctional bismaleimide monomer can be thermally cured to create the crosslinked network matrices with excellent thermal and chemical resistances and mechanical properties. The preparation and characterization of bismaleimide-based composite materials can be found in Refs. 6–9.

Pan et al.[10] studied the free radical polymerizations of N,N′-bismaleimide-4,4′-diphenylmethane (abbreviated as BMI) initiated by barbituric acid (BTA). The resultant hyper-branched BMI polymers were more soluble in organic solvents compared with the crystalline BMI monomer. To the best of the authors' knowledge, the literature dealing with the reaction mechanisms and kinetics of the polymerizations of BMI using BTA as the free radical generator is rather limited.

The effects of solvent on the free radical polymerization kinetics of N-substituted maleimides initiated by 2,2′-Azobis(isobutyronitrile) (AIBN) were investigated.[11,12] Chain transfer of radicals to solvent played an important role in the reaction kinetics. Matsumoto et al.[13] reported that benzene was the solvent of choice in terms of polymer yield and molecular weight for the polymerization of N-(alkyl-substituted phenyl)maleimides using AIBN as the initiator at 60°C, when compared with N,N-dimethyl formamide (DMF). It was also reported that, for the polymerization of maleimide initiated by dimethyl 2,2′-azobisisobutyrate at 60°C, both the polymer yield and molecular weight in decreasing order was in chloroform > methyl benzoate > 1,2-dichloroethane > benzene > anisole > dioxane, expect for the polymerization in chloroform that results in a smaller molecular weight.[14] Polymerization of N-cyclododecylmaleimide was initiated by AIBN in several solvents including tetrahydrofuran, toluene, benzene, and dioxane. Based on the data of polymers yield and molecular weight, benzene was the best for the

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polymerization of N-cyclododecylmaleimide.[15] The copolymerization rate of cyclohexene with N-phenyl-maleimide was carried out with AIBN as an initiator in benzene at 50°C is higher than that in chloroform and in dioxane.[16]

To the best knowledge of the authors, the literature dealing with the effect of solvents on the free radical polymerization of bismaleimide initiated by barbituric acid was nil. The aim of this work was to use measurements of gel content, polymer molecular weight and molecular weight distribution, and polymer solution viscosity to study the effects of solvents with different chemical structures on the free radical polymerization of BMI initiated by BTA. Under exactly the same experimental conditions, a higher level of insoluble polymer species (i.e., gel content) produced during the reaction then reflects a more active free radical polymerization system. The results obtained from this study may help gain a better understanding of the BMI polymerization mechanisms and kinetics. A mechanism that takes into account the formation of radical pairs in the initiation step and their subsequent propagation reactions with BMI monomer molecules will be presented in this article.

EXPERIMENTAL

Materials

The reagents used in this work include N,N′-bismaleimide-4,4′-diphenylmethane with a purity of 95.8% (Hakuei & Co., Japan), barbituric acid (Merk), N,N-dimethylacetamide (DMAC, Acros), N,N-dimethyl formamide (Mallinckrodt), N-methyl-2-pyrrolidinone (NMP, Sigma), N-ethyl-2-pyrrolidinone (NEP, Acros), N-butyl-2-pyrrolidinone (NBP, TCI), N-dodecyl-2-pyrrolidinone (NDP, Aldrich), γ-butyrolactone (GBL, Acros), and 2-pyrrolidinone. All chemicals were used as received.

Polymerization and characterization

The gel content test samples obtained from the free radical polymerizations of BMI initiated by BTA in a variety of solvents were carried out in a sealed 7-mL glass vial with magnetic mixing in an oil bath thermostatically controlled at 130°C for 6 h. The total solids content of the reaction system was kept constant at 20% throughout this work.

About 0.6 g of the resultant polymer solution sample was diluted with 6 g of GBL and magnetically stirred at room temperature for 48 h. This was followed by filtration with a 200-mesh screen to obtain the insoluble moiety. The screen was then dipped in an excess of GBL at room temperature for 24 h to remove the entrapped soluble species such as resid-ual BMI monomer and BTA initiator and soluble polymer. Finally, the insoluble polymer species was obtained by drying the screen in a vacuum oven at 150°C for 24 h. The reported gel content is defined as the weight percentage of the insoluble polymer species.

For gel permeation chromatography (GPC) and rheology measurements, the BMI polymer solution samples were prepared by the polymerizations with a molar ratio of BTA to BMI (BTA/BMI) at 1/4 in the solvent mixtures of NMP and GBL in a 250-mL three-neck reactor equipped with a magnetic stirrer and a reflux condenser in a oil bath thermostatically controlled at 130°C for 6 h. The reaction temperature was kept constant at 128.7 ± 0.8°C throughout the polymerization.

The relative molecular weights and molecular weight distributions of some of the resultant polymers were determined by GPC equipped with four columns (Shodex KD-801, KD-8025, KD-804, and KD-805 ultrastyragel) in series and a RI detector (Jasco-830RI). DMF was used as the eluent solvent at 40°C and a flow rate of 0.8 mL/min was used for the molecular weight measurements. Four polystyrene standards (molecular weights = 1.25×10^5, 2.26×10^5, 5.64×10^5, and 1.07×10^{-6} g/mol) supplied by PSS Polymer Standards Service Gmbh were used to establish the calibration curve. As will be shown in the section Results and Discussion, extrapolation was required to obtain the molecular weight and molecular weight distribution data. The rheological properties of the resultant polymer solution samples with a total solids content of 20% at 25°C were measured by a strain-controlled rheometer with a parallel plate geometry (diameter = 50 mm, gap = 0.4 mm, shear rate = 1–1000 1/s) (TA Instruments AREL-LS1, New Castle, DE). All the samples showed a shear-thinning behavior and only the stationary viscosity (η) data at 1000 1/s were reported in this article.

RESULTS AND DISCUSSION

Polymerization and characterization

The chemical structures of the solvents chosen for study are shown in Scheme 1. Figure 1 shows that the polymerizations carried out in the nitrogen-containing cyclic NMP resulted in the highest gel contents, even in the region of lower molar ratios of BTA to BMI (see the square data points). By contrast, the cyclic GBL containing no nitrogen atoms gave nil gel contents upto a molar ratio of BTA/BMI equal to 1/4 (see the circular data points in Fig. 1). The difference in gel contents may be attributed to the nitrogen-containing cyclic structure (an electron-rich structure) that serves as a Bronsted base,
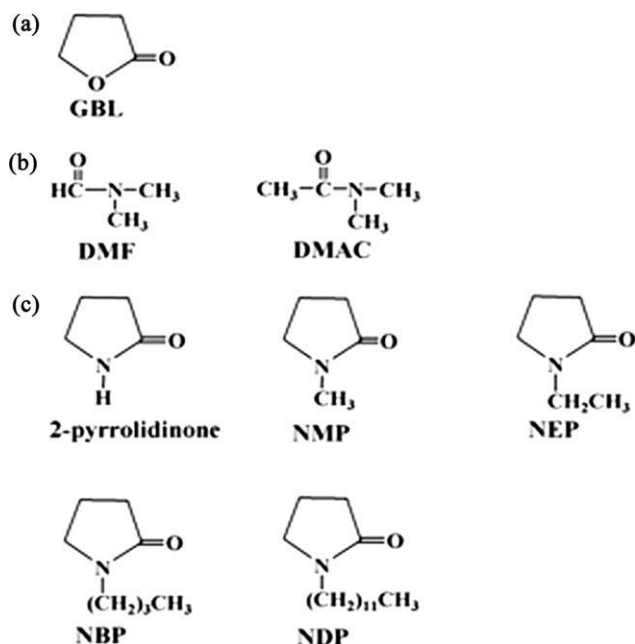
Scheme 1 Chemical structures of a variety of solvents chosen for study: (a) cyclic structure in the absence of nitrogen, (b) noncyclic structures containing nitrogen, and (c) cyclic structures containing nitrogen.

thereby acting as a catalyst to promote the vigorous free radical polymer reactions (i.e., the gelling process). The basicity of those solvents having a nitrogen-containing cyclic chemical structure (e.g., NMP) is stronger compared with those having a cyclic structure in the absence of nitrogen (e.g., GBL) or those having a noncyclic structure in the presence of nitrogen (e.g., DMF and DMAC). Figure 1 shows that the tendency for the polymerizations over a wide range of BMI and BTA concentrations to form insoluble polymer species in decreasing order is
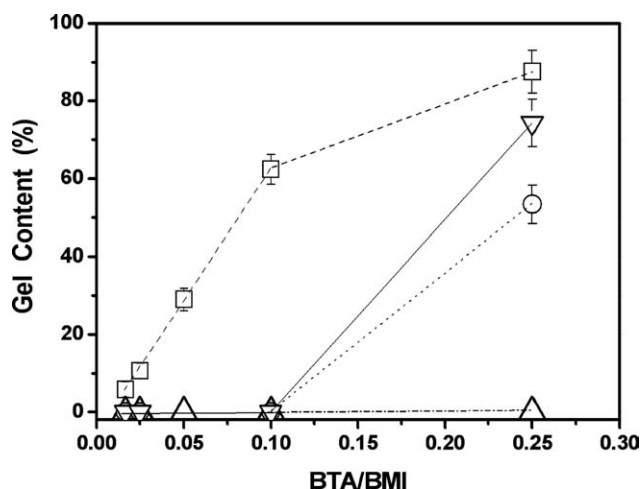

Figure 1 The gel content data as a function of the molar ratio of BTA to BMI (BTA/BMI) for the polymerizations of BMI initiated by BTA and carried out in different solvents: (□) NMP, (△) GBL, (○) DMF, and (▽) DMAC.
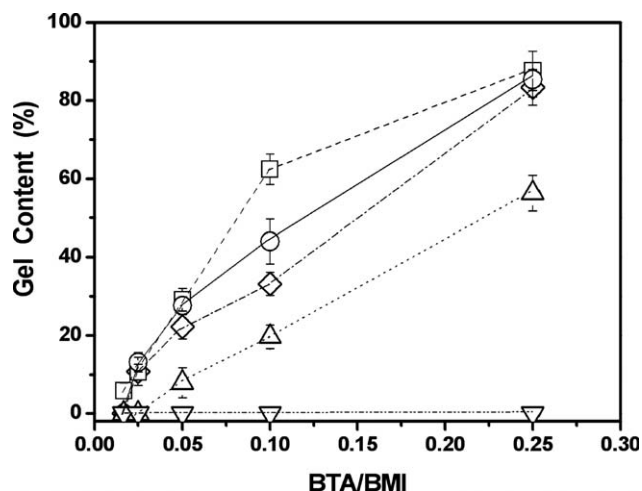
Figure 2 The gel content data as a function of the molar ratio of BTA to BMI (BTA/BMI) for the polymerizations of BMI initiated by BTA and carried out in different solvents: (◇) 2-pyrrolidinone, (□) NMP, (○) NEP, (△) NBP, and (▽) NDP.

NMP > DMAC > DMF > GBL. It seems that the solvent basicity governs the gel formation process for the BMI polymerizations initiated by BTA.

To verify the above speculation, a series of polymerizations using the nitrogen-containing cyclic solvents shown in Scheme 1(c) were carried out. The major parameter chosen for study is the chain length of the alkyl group ($-C_nH_{2n+1}$, $n = 0, 1, 2, 4, 12$) attached to the nitrogen atom. The alkyl chain length is expected to have an effect on the solvent basicity. First, the solvent basicity generally increases with increasing alkyl chain length, as illustrated by the pK_a values of alkylamines ($C_nH_{2n+1}-NH_2$, $n = 1-4$, 6, 8) in water at 25°C compiled in Ref. 17. On the other hand, the solvent basicity also can be reduced to some extent by the increased alkyl chain length due to the steric hindrance to solvation, as evidenced by the pK_a values of N-alkylpiperidine ($C_5H_{10}N-C_nH_{2n+1}$, $n = 1, 2, 4$).[17] Thus, an optimal alkyl chain length that leads to the highest solvent basicity might exist in this set of experiments. The experimental results are shown in Figure 2, and the level of gel content in decreasing order is NMP > NEP > 2-pyrrolidinone > NBP >> NDP. This trend is in qualitative consistence with the theoretically predicted solvent basicity, and the results obtained from this set of independent experiments further support the above postulation that solvent basicity plays a crucial role in the BMI polymerizations initiated by BTA. The stronger the solvent basicity, the more reactive the BMI polymerization system. It is noteworthy that the molar ratio of BTA to BMI also shows a significant influence on the level of gel content (Figures 1 and 2).

It is of great interest to quantitatively determine the effectiveness of solvents in promoting the
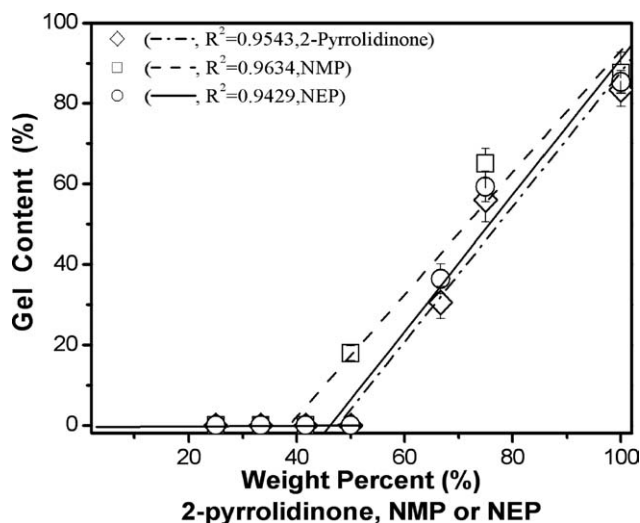
Figure 3 The gel content data as a function of the weight percentage of the nitrogen-containing solvents in the two-component solvent systems for the polymerizations of BMI initiated by BTA with the molar ratio of BTA to BMI (BTA/BMI) equal to 1/4 and carried out in different solvent mixtures: (◇) 2-pyrrolidinone/GBL, (□) NMP/GBL, and (○) NEP/GBL.

formation of the crosslinked network structure for the BMI polymerizations with BTA as the initiator. To demonstrate one potential approach shown below, three nitrogen-containing cyclic solvents, 2-pyrrolidinone, NMP, and NEP, in combination with GBL that did not exhibit any catalytic effect were chosen for investigation. In this set of polymerizations, the molar ratio of BTA to BMI (BTA/BMI) was kept constant at 1/4. A general feature of the experimental data shown in Figure 3 is that the gel content first remains relatively constant (about zero) when the weight percentage of a particular nitrogen-containing cyclic solvent in the reaction medium increases from 25% to about 50% (Interval I). This is followed by the rapidly increased gel content with the weight percentage of the nitrogen-containing cyclic solvent (Interval II). Based on the least-squares best-fit method, the intersection between the two straight lines identified in Intervals I and II, respectively, was defined as the critical point for the first appearance of insoluble polymer species. The data of the critical point of the straight line in Interval II thus obtained are listed in Table I. The smaller the critical point, the stronger the catalytic effect of the nitrogen-containing cyclic solvent. Based on these experimental data, the effectiveness of the nitrogen-containing solvents in producing insoluble polymer species in decreasing order is NMP > NEP > 2-pyrrolidinone, which is in good agreement with the results shown in Figures 1 and 2.

The BMI polymer solution samples obtained from the polymerizations carried out in 25.0, 33.3, and 41.7 wt % of NMP in the solvent mixtures of NMP

TABLE I
Critical Point for the First Appearance of Insoluble Polymer and the Slope Obtained from the Least-Squares Best Fitted Straight Line in Interval II for the Polymerizations of BMI Initiated by BTA with the Molar Ratio of BTA to BMI (BTA/BMI) Equal to 1/4 and Carried Out in Different Solvent Mixtures

Solvent system	Critical point (%)
2-Pyrrolidinone/GBL	47.6
NMP/GBL	38.6
NEP/GBL	46.2

and GBL before the appearance of gelation (Fig. 3) were selected for the molecular weight measurements. The characteristic peaks of GPC elution curves correspond to BMI polymer, BMI monomer, and solvents, respectively (Fig. 4). For comparison, the GPC elution curves for the neat BMI monomer is also included in this plot. The retention times of 25.5 and 47.5 min represent the molecular weight of the resultant BMI polymer and the residual BMI monomer, respectively. Thus, the ratio of the integrated peak area of the BMI polymer to that of the residual BMI monomer (A_P/A_M) can be estimated and the results are listed in Table II. The higher the A_P/A_M ratio, the greater the monomer conversion is. It is shown that the BMI polymer content (i.e., the fraction of BMI monomer initially present in the reaction system that is ultimately incorporated into the polymer) increases with increasing weight percentage of NMP in the solvent mixture. It is quite unusual that
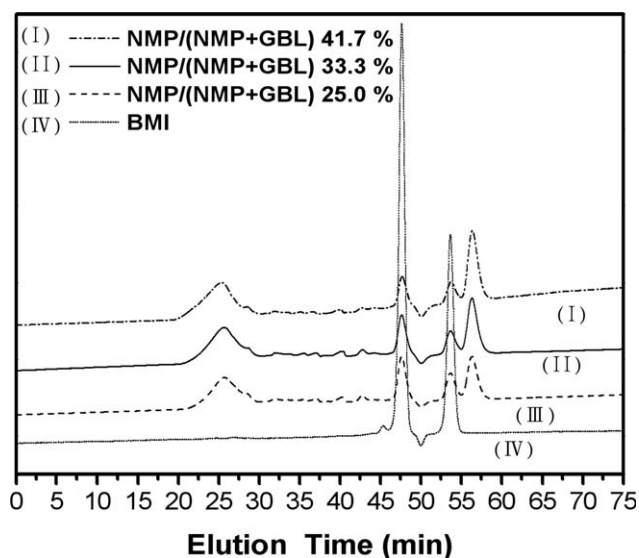

Figure 4 The GPC elution curves of the BMI polymers obtained from the polymerizations of BMI initiated by BTA with the molar ratio of BTA to BMI (BTA/BMI) equal to 1/4 and carried out in the solvent mixtures of NMP and GBL. For comparison, the spectrum of BMI monomer is also included in this plot (see curve IV). The weight percentage of NMP in the solvent mixtures is as follows: (I) 41.7%, (II) 33.3%, and (III) 25.0%.

NMP (wt %)[a]	A_P/A_M	$M_w \times 10^{-6}$ (g/mol)	M_w/M_n
25.0	2.11	5.69	1.47
33.3	2.50	6.33	1.54
41.7	3.46	8.17	1.64

[a] wt % of NMP in the mixture of NMP and GBL.

a significant amount of the difunctional monomer BMI can survive the free radical polymerizations initiated by BTA at 130°C (see the GPC elution curves at 47.5 min in Fig. 4). This is most likely due to the rather inefficient BTA in initiating the polymer reactions. More research is required to clarify the BTA-initiated BMI polymerization mechanisms and kinetics.

It is also very interesting to note that the weight-average molecular weight (M_w) increases with increasing weight percentage of NMP in the solvent mixtures of NMP and GBL (Table II). Recall that both the molar ratio of BTA to BMI and reaction temperature remains unchanged in this series of polymerizations. Under these circumstances, the M_w data are not expected to vary to any appreciable extent according to conventional free radical polymerization mechanisms (molecular weight is proportional to $[BMI]/[BTA]^{1/2}$, where [BMI] and [BTA] represent the concentrations of BMI and BTA, respectively), provided that other parameters do not come into play in the reaction mechanisms. However, it has been shown in this study that the solvent basicity has a significant effect on the BMI polymerization behavior. As a result, the BMI polymers prepared by the polymerizations carried out in different solvent mixtures should exhibit different molecular weights and molecular weight distributions. Indeed, Figure 5 shows that the weight-average molecular weight (M_w) is proportional to the weight percentage of NMP in the solvent mixture (P_{NMP}) to the 0.69 power ($M_w \sim P_{NMP}^{0.69}$). It is also shown in Figure 5 that the stationary viscosity (η) data obtained from the polymer solutions at a total solids content of 20% is proportional to the weight percentage of NMP in the solvent mixture to the 1.85 power ($\eta \sim P_{NMP}^{1.85}$). This trend further supports the postulation that solvent basicity plays an important role in the BMI polymerizations initiated by BTA. For linear polymers with $M_w = 10^7$ g/mol, the viscosities of polymer solutions at a total solids content of 20% are generally very high. Thus, the magnitudes of the stationary viscosity data (1.77×10^{-2} to 4.59×10^{-2}

Pa s) determined in this work imply that the rheological behavior of the resultant BMI polymers is quite different from linear polymer solutions. The M_w data in the range 5.7×10^6–8.2×10^6 g/mol determined by GPC should be regarded as qualitative only because the linear polystyrene standards were used to establish the calibration curve. Nevertheless, these M_w and η data imply that the resultant BMI macromolecules exhibit relatively large hydrodynamic sizes, high volume fractions of interior void, and excellent flow properties, which are the typical characteristics of hyper-branched polymers. It should be noted that the above empirical equations should be regarded as qualitative only due to the rather limited number of data points available for each series of experiments.

Finally, the polydispersity index defined as M_w/M_n (centered about 1.5), where M_n is the number-average molecular weight, does not change very much when the NMP content in the solvent mixture is increased (Table II). These molecular weight distribution data are below the lower limit of the reported polydispersity index values (in the range 2–5) for free radical polymerizations.[18] Thus, the BMI polymerizations using BTA as the initiator resulted in polymer products with much narrower molecular weight distributions when compared with conventional free radical polymerization systems. The GPC and rheological data, again, provide supporting evidence of the role of the nitrogen-containing cyclic solvents in the BTA-initiated polymerization of BMI.

Polymerization mechanisms

Based on the experimental results presented in this work, a model describing the BMI polymerization
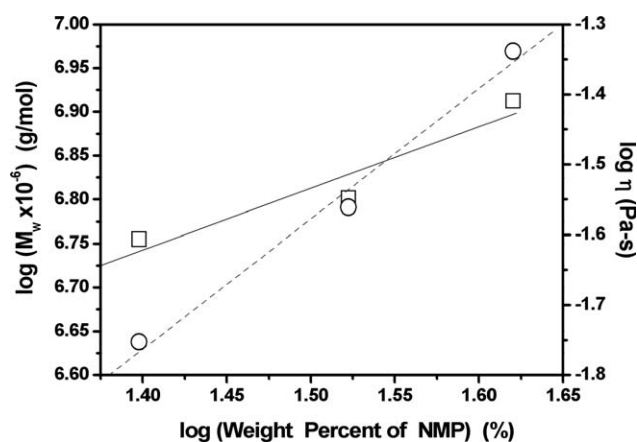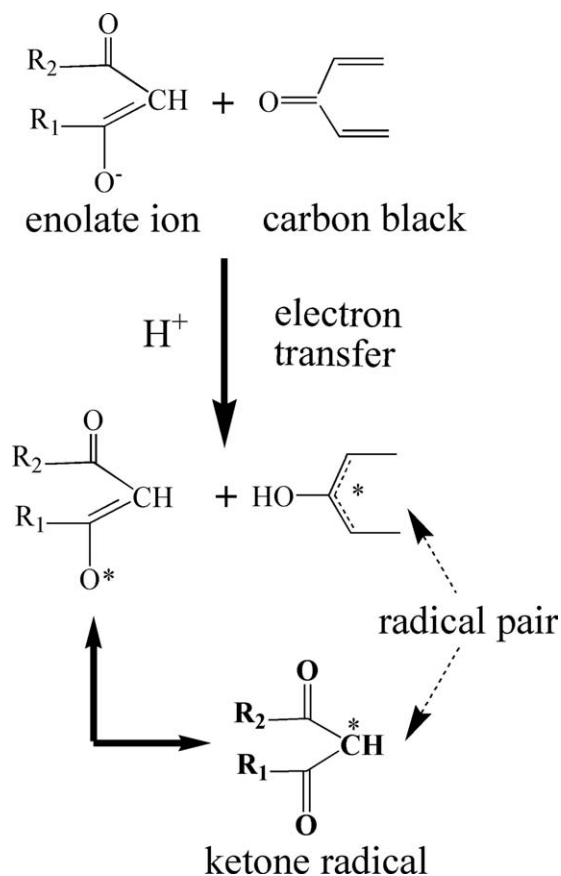
Figure 5 The weight-average molecular weight (□) and the stationary viscosity of polymer solutions at a total solids content of 20% (○) as a function of the weight percentage of NMP in the two-component solvent systems of NMP and GBL for the polymerizations of BMI initiated by BTA with the molar ratio of BTA to BMI (BTA/BMI) equal to 1/4.

**Scheme 2** Mechanism of formation of a ketone radical pair via the single electron transfer process.[19]

initiated by BTA was developed in this study. Tsubokawa et al.[19] studied the free radical polymerizations of methyl methacrylate initiated by an enolizable ketone (R_1—CO—CH_2—CO—R_2) in combination with carbon black. They proposed a mechanism for the formation of a ketone radical pair via the single electron transfer reaction from enolate ion to the quinonic oxygen group, as shown in Scheme 2. It was shown that the extent of polymer crosslinking reactions for the systems carried out in different solvents in decreasing order is NMP > DMF > dimethyl sulfoxide > 1,4-dioxane > benzene. On the basis of the pioneering work of Tsubokawa et al.,[19] we postulated that the free radical polymerization begins with the formation of a ketone radical pair via the reaction between BTA and BMI. This is followed by the reaction of this ketone radical pair with one BMI molecule to generate a primary radical pair [Scheme 3(a)]. This initiation mechanism also leads to the speculation that the nitrogen-containing cyclic solvent species may act as a catalyst in the formation of ketone radical pairs and, thus, promote the strong free radical polymerization. Solvent molecules with high basicity surrounding the two neighboring BTA and BMI molecules may facilitate their rearrangement into an adequate position that promotes the

single electron transfer process. However, the exact reaction mechanisms associated with the role of solvents with high basicity in the BMI/BTA polymerizations are not clear at this point of time.

The primary radical can attack another BMI species to form a propagating radical pair [Scheme 3(b)]. The propagation reactions include the addition of the maleimide group of a free BMI molecule or the pendant maleimide group attached to a polymer chain to the active polymer chain end radical. The propagation reactions proceed until the termination reactions occur. It should be noted that both the initiation and propagation steps are regarded as equilibrium reactions because the polymerization temperature (130°C) is quite high. The bimolecular termination reaction between two proximately approaching polymer chain radicals is shown in Scheme 3(c). The resultant BMI polymer presumably has a structure depicted in Scheme 3(d). In addition to the termination reaction, the dimension of this hyper-branched structure also depends on the equilibrium constants of the propagation reactions. For example, gigantic polymers with a three-dimensional (3D) network structure can be achieved when the rate of the forward propagation reaction rate is much faster than that of the backward reaction and/or the termination rate constant is relatively small. On the other hand, low-molecular-weight oligomers with a hyper-branched structure are likely the products when the rate of the backward reaction is comparable to that of the forward propagation reaction and/or the termination rate constant is very large. Furthermore, the polymer reactions involving neighboring macromolecules have a crucial effect on the evolution of molecular weight and molecular weight distribution of the BMI-based polymerizations. These intermolecular reactions result in a rapid increase in the polymer molecular weight and promote the formation of the 3D crosslinked network structure. Research work on the BTA-initiated BMI polymerization mechanisms and characterization of the resultant polymers is in progress in our laboratories.

CONCLUSIONS

The effects of solvent basicity on the free radical polymerizations of N,N'-bismaleimide-4,4′-diphenylmethane (BMI) initiated by barbituric acid (BTA) at 130°C were investigated. The results obtained from measurements of gel content, polymer molecular weight, and polymer solution viscosity suggested that the nitrogen-containing cyclic solvents such as N-methyl-2-pyrrolidinone acted as a catalyst to promote the BMI polymer reactions. As a consequence, very high levels of gel content were obtained from the reaction products. On the other hand, the BMI polymerizations carried out in a cyclic solvent that
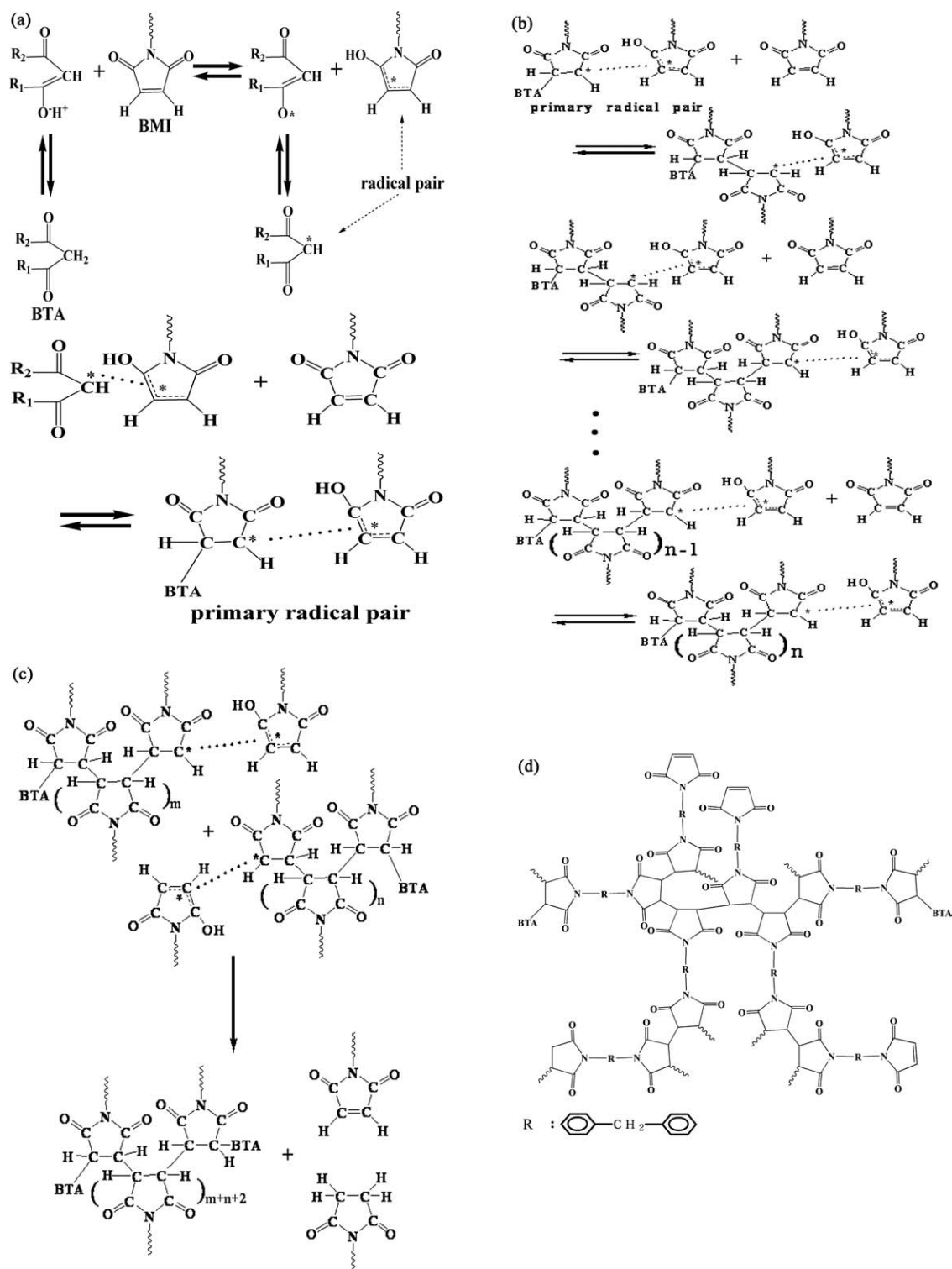
Scheme 3 Mechanisms of free radical polymerization of BMI initiated by BTA: (a) initiation reactions, (b) propagation reactions, (c) termination reactions, and (d) a representative molecular structure of the resultant BMI polymer.

did not contain nitrogen, γ-butyrolactone, resulted in nil insoluble polymer species. A method was developed to determine the critical point for the first appearance of insoluble polymer species. It was concluded that higher the solvent basicity, stronger the

effect of the solvent in promoting the formation of the 3D crosslinked network structure. Furthermore, as would be expected, the molar ratio of BTA to BMI also showed a significant influence on the formation of insoluble polymer species. In general, the

gel content increased with increasing molar ratio of BTA to BMI. The resultant BMI polymers, presumably having a hyper-branched structure, showed much narrower molecular weight distributions than those prepared by conventional free radical polymerizations.

The experimental results obtained from this study implied that the BMI polymerizations using BTA as the initiator could not be adequately described by conventional free radical polymerization mechanisms. Thus, a polymerization mechanism that took into consideration the generation of a ketone radical pair between the neighboring BTA and BMI molecules and the subsequent initiation, propagation, and termination reactions was proposed. It was postulated that the nitrogen-containing cyclic solvents were capable of participating in the ketone radical pair formation process, thereby accelerating the free radical polymerization.

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