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Direct ether formation of semibenzopinacol moieties in a photopolymerization system featured constant intensity of absorbed light

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Abstract

In a special photopolymerization reaction system, the reactivity of semibenzopinacol moieties was examined. Structural analysis by 1D/2D NMR showed that the hydroxyl groups of the semibenzopinacol moieties after hydrogen abstraction reaction have reacted directly to form a new ether structure instead of the cleavage of a C–C bond in a photopolymerization system featured constant intensity of absorbed light when there is only vinyl acetate added. In order to clarify this new reaction, comparative experiments and several characterization methods were applied. Results revealed that poly(vinyl acetate) radicals initiated by UV irradiation or benzophenone/triethanolamine system, and UV irradiation under or above 300 nm, were two necessary factors for the formation of the new ether structure from hydroxyl groups of semibenzopinacol moieties.

Keywords: Semibenzopinacol moiety; Ether; Photopolymerization; Vinyl acetate; Benzophenone; Triethanolamine

1. Introduction

Benzophenone with its effective hydrogen abstraction reaction has served actively not only in the fields of photopolymerization [1–5], polymeric surface modification [6–11] and photocrosslinking [12,13] but also as a new polymeric photosenitizer [14] and a new analytical technique [15]. However, the characterization of exact structures of final products and corresponding formation mechanisms in these systems are very limited [16,17] and mostly not satisfactory enough.

Recently, we carried out a detailed analysis of the final structures of benzophenone related products by 1D/2D NMR techniques [18]. Notably, two new structures (Structures 1 and 2 in Scheme 2) were revealed from a newly-designed photopolymerization reaction system featured relatively constant intensity of absorbed light. One common characteristic of them is a new ether structure (Structure 1/2

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in Scheme 2) formed when benzophenone and vinyl acetate served as the only reactants under UV irradiation. However, how the new ether structure, seemingly a derivative from the hydroxyl group of semibenzopinacol moiety [19,20], was formed is still unclear. It is therefore essential to understand the reactivity of semibenzopinacol moieties [21,22]. This is not only because these moieties are immediate products of benzophenone's hydrogen abstraction reaction that is comprehensively utilized [1–15], but also because benzopinacolate has been applied as a new class of thermal initiator for "living/controlled" polymerization, whose initiation comprises thermal dissociation of a C–C bond [19,23–28]. In short, it is very significant to clarify the formation of the new ether structure or more specifically, the reactivity of semibenzopinacol moiety in macromolecular system.

This report focuses on the formation of the new ether structure, actually examining the reactivity of the semibenzopinacol moiety in this unique reaction system through several comparative experiments. In the meantime, exact structures of the products are also directly examined with 1D/2D NMR [29,30]. The application of these high-resolution instruments and specific experiments enables us to harvest more details of the structure and the discovery of a completely new reaction of semibenzopinacol moieties.

2. Experimental

2.1. Materials

BOPP film (biaxially oriented polypropylene) with a thickness of approximately 30 μm was used as a sliding medium upon, but close to, the top of the setup in the experiments (Fig. 1). Benzophenone (BP) was used as received from Academy of Military Medical Science, China. Triethanolamine (TEOA), acetone and ethanol were used as received from Beijing Chemical Reagents Co. Ltd., China.

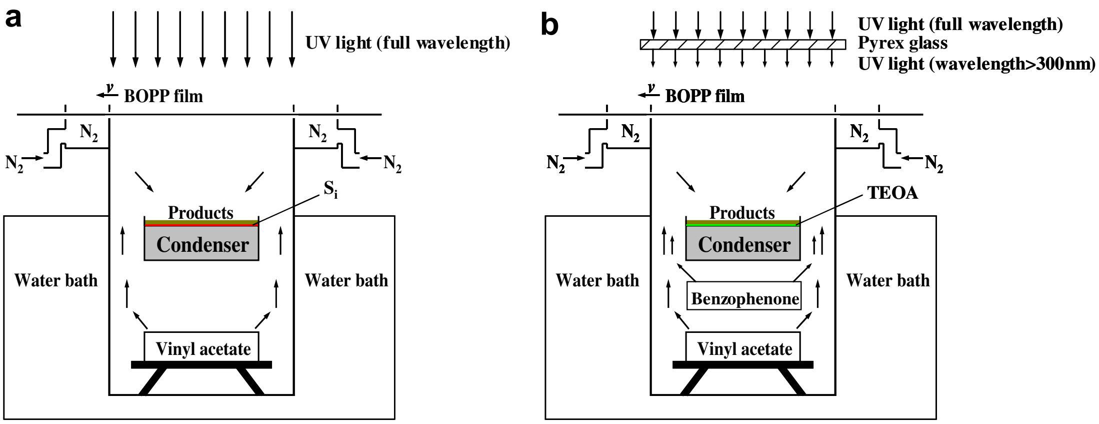
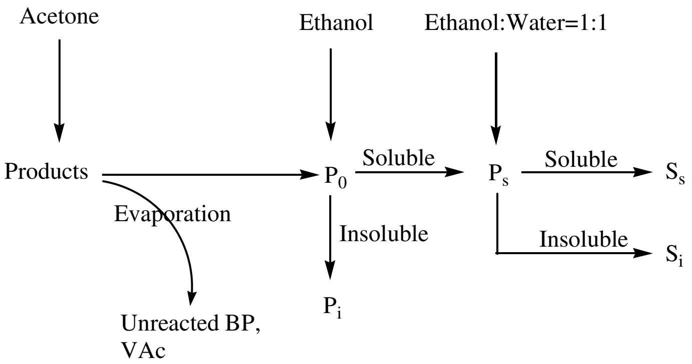


Fig. 1. Reaction systems. (a) Reaction system for Experiment 1; (b) reaction system for Experiment 3.



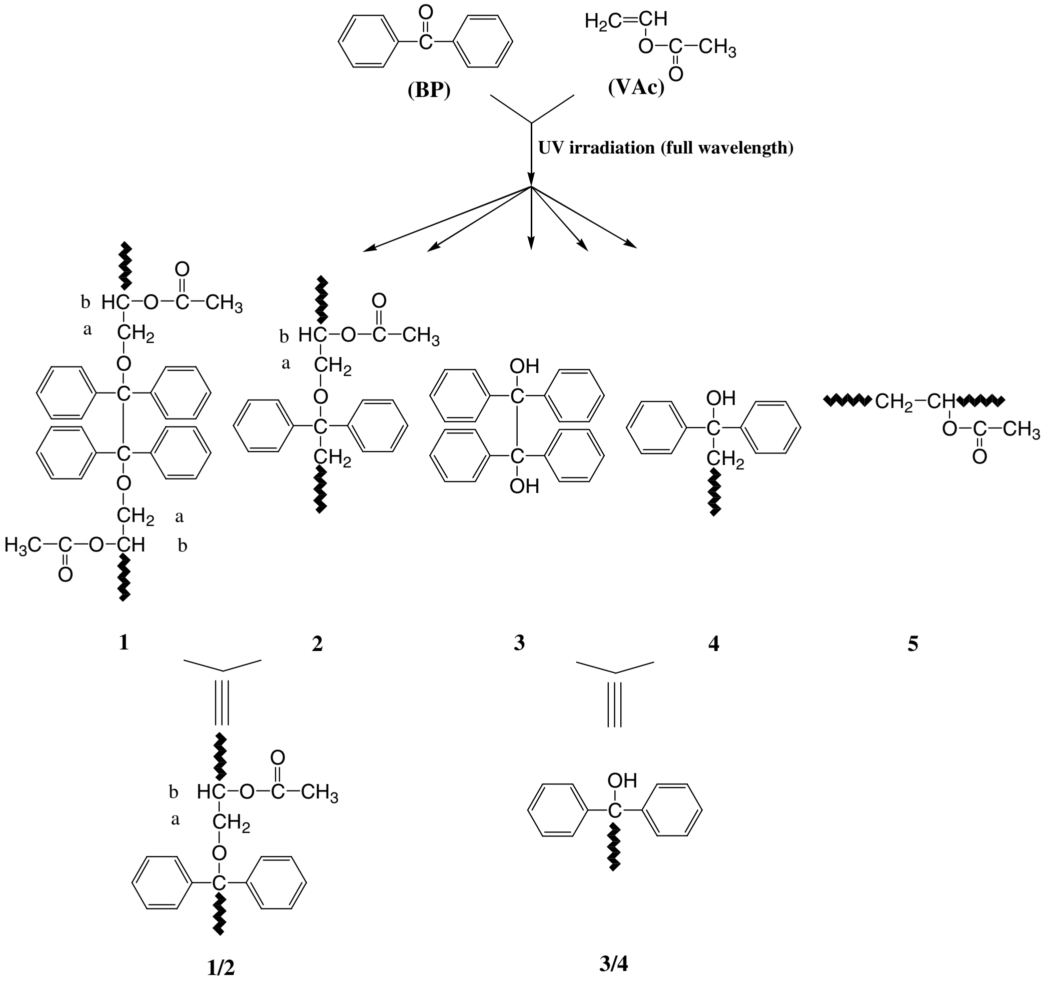
Scheme 1. Separation procedures.

The deionized water used has a conductance of 0.5 μs cm^{-1}. Vinyl acetate (VAc) was distilled and purified under reduced pressure before use.

2.2. Polymerization and separation

A new reaction system featured relatively constant intensity of absorbed light was designed for photopolymerization [18]. It achieves a constant transmission of UV light into the system and follows partly a gas phase polymerization-like pathway. The reactions mainly happened in gas phase and on the top of the condenser and products were collected in the upper vessel of the condenser. Especially on the condenser, both heating effect and screening effect of UV light were removed.

Before assembly of the reaction system and the polymerization here, another polymerization was carried out as depicted in Ref. [18] at first. Ethanol soluble proportion P_s (separation procedures in Scheme 1) of a sample obtained in a similar reaction system [18] (vinyl acetate at 30 °C (±0.1 °C), benzophenone at 135 °C (±0.1 °C), condenser at 10 °C (±0.1 °C), water bath at 90 °C (±1 °C) and reaction time 3 h) was separated with a mixed solvent of water and ethanol (v:v = 1:1) into another two parts: the soluble part (S_s, soluble part of the previously soluble proportion) and the insoluble part (S_i, insoluble part of the previously soluble proportion). S_i was isolated and dried at 60 °C and in vacuum until it achieved a constant weight. After NMR measurement, 5 mg of S_i was weighted and dissolved with 0.3 ml acetone and then the solution was injected into the top vessel of the condenser in the reaction system. When the acetone was fully vaporized, the reaction system was assembled as



Scheme 2. A summary of the reaction scheme revealed in the previous report [18].

Table 1
Conditions of five comparative experiments

Experiments	Components	UV light	Time (h)	Temperatures (°C)		
				BP	Condenser	VAc
1	S_i, VAc	No filter	1	–	10	40
2	S_i, VAc	Pyrex filtered	1	–	10	40
3	BP, TEOA, VAc	Pyrex filtered	1	110	10	40
4	BP, VAc	Pyrex filtered	3	–	–	40
5	VAc	Pyrex filtered	3	–	–	40

depicted in Fig. 1a and pure nitrogen gas was introduced into the apparatus, and then transferred to the circle around the top of the apparatus before irradiation to form an oxygen-expelling buffer with a gas flow of about 15 $cm^3\ s^{-1}$, which was maintained during irradiation. After these, temperatures of different components were set and 10 min later the whole apparatus was exposed to UV irradiation. Vinyl acetate was controlled at 40 °C (±0.1 °C), while condenser at 10 °C (±0.1 °C), water bath at 90 °C (±1 °C) and reaction time 1 h. After reaction, P_s was obtained following the procedures in Scheme 1 and was then characterized with instruments needed. Brief description of the conditions could be found in Table 1 (Experiment 1), where also lists those for the following experiments.

As a contrast to the experiment above, a comparative experiment was carried out with only one difference: during the polymerization or irradiation, a 2 mm thick Pyrex glass was placed over the BOPP film to filter UV light lower than 300 nm (Experiment 2 in Table 1). For Experiment 3, the procedures were also very similar to those depicted in Ref. [18]. Besides a 2 mm thick Pyrex glass was applied as that in Experiment 2, the only difference is that 0.2 ml acetone solution of triethanolamine (TEOA) with a concentration of 2.7×10^{-8} mol/ml was first injected on top vessel of condenser and then fully evaporated (Fig. 1b). The temperature of BP was controlled at 110 °C (±0.1 °C). For Experiment 4, the procedures were very similar to those for Experiment 2 but without the involvement of S_i and the reaction time was 3 h. For Experiment 5, the procedures were very similar to those for Experiment 4 but without the involvement of BP.

In this report, we continue to use vinyl acetate as monomer as the previous one in the system mainly because of its representative structure as hydrogen donors for benzophenone (with all primary, secondary, tertiary hydrogen atoms), relatively higher vapor pressure than many common vinyl monomers [31], long-time stability under mild thermal conditions and agreement with the previous report, lowering the chances of complicated NMR spectra brought when other vinyl monomers are applied.

2.3. Characterization methods

All NMR spectra, ^{1}H, ^{1}C, DEPT-135 (Distortionless Enhancement by Polarization Transfer), HSQC (Heteronuclear Single-Quantum Correlation) and HMBC (Heteronuclear Multiple-Bond Correlation), were collected on a Bruker Avance 600 spectrometer at room temperature on a 5–25 mg sample in 0.5 cm^3 of acetone-d_6; wherein, HSQC and HMBC were obtained on the instrument equipped with a 5 mm indirect detection probe and waveform generator (used to accomplish GARP decoupling in indirect detection experiments). All data were processed with Bruker's XWIN-NMR software. For detailed description of the setting of parameters in 1D/2D NMR, refer to Ref. [18]. Molecular weights and molecular weight distributions were determined with a GPC instrument (Waters) equipped with a series of Styragel columns (HT3, HT5, and HT6E), a refractive-index (RI) detector (Waters 2410), and a UV detector (Waters 996 photodiode array detector). M_n and M_w/M_n were calculated on the basis of versatile calibration by the k (3.5×10^{-4}) and α (0.63) of PVAc. UV–vis spectra of were recorded in ethanol solution on a GBC Cintra-20 spectrophotometer (GVC Scientific Equipment Pty Ltd., Dandenog, Australia).

3. Results and discussion

In our previous report [18], two new structures (Structures 1 and 2), summarized as Structure 1/2 in Scheme 2, were comprehensively confirmed. It is very likely that this ether structure was formed after reactions between semibenzopinacol moieties (Structure 3/4 in Scheme 2) and other reactants or intermediates (the first assumption). Therefore, in the first part of this report, semibenzopinacol moieties of benzopinacol and semibenzopinacol-connected poly(vinyl acetate) were directly exposed to a similar chemical environment so as to examine immediately whether this assumption is right or not.

3.1. Direct ether formation from hydroxyl groups on semibenzopinacol moieties

The ratio of ethanol to water to obtain S_i from P_s for comparative Experiments 1 and 2 (Table 2, corresponding with Table 1), 1:1 (v:v), was optimum after testing with different values. With this ratio, the S_i happened to have no resonances in the regions of 4.55–4.70 ppm and 5.90–6.10 ppm (Fig. 2A), for groups a and b of Structure 1/2 in Scheme 2, respectively, representing no hydroxyl group of semibenzopinacol moieties on benzopinacol or semibenzopinacol-connected poly(vinyl acetate) reacted to form ether. Therefore, S_i could be used for the investigation of the reactivity of semibenzopinacol moieties in this photopolymerization system. Here, S_i is mainly a mixture of benzopinacol and semibenzopinacol-connected poly(vinyl acetate) as indicated in previous report [18] and in Fig. 2A, since there were two peaks in the GPC spectrum, one at approximately 300 while the other about 1900 (Table 2). In the rest of this report, semibenzopinacol moieties are used as representative of these two structures, as shown in Scheme 2, Structure 3/4.

^{1}H spectrum of P_s of the products from Experiment 1 is shown in Fig. 2B, while that from Experiment 2 was the same as those in Fig. 2A, which means that there was no reaction is Experiment 2; more importantly, compared with Fig. 2A, the phenyl region in Fig. 2B at 7.0–8.0 ppm changed a lot inside, such as the advent of resonances at 7.61–7.65 ppm and an obvious but relative increase of resonances at 7.20–7.40 ppm. Because there were no BP and other reactants with phenyl groups besides semibenzopinacol moieties from S_i in the system, the change could only come from the reaction of benzopinacol itself or with other products/intermediates during the experiment, namely a cleavage of semibenzopinacol moieties from the rest parts or some other reactions. Peaks at 4.59–4.62 (H-a(1)) and 5.97–5.99 (H-b) ppm in ^{1}H spectrum in Fig. 2B and 70.8(C-a) and 73.7(C-b) ppm in ^{1}C spectrum in Fig. 3B are identical to those reported previously [18] but still need to be assured accurately and there are some other newly appeared ones to be confirmed. In order to make clear what structures were obtained and then study the reactivity of semibenzopinacol moieties through comparative experiments afterwards, 2D NMR was utilized.

Full HMBC spectrum of P_s from Experiment 1 (Fig. 4A) is very similar to that in previous report [18] although through a different reaction route, representing that structures obtained here are very close to Structure 1 or 2 previously reported (Scheme 2). Further analysis of the spectra, C-b was found to correlate with both H-a(1) at 4.59–4.62 ppm and H-t at 3.27–3.33 ppm (Fig. 4A and B). HSQC spectrum of the product indicated that C-t was at 58.2 ppm. Because C-b here is a chiral atom and thus H-a(1) and H-a(2) were not equal, it is logical to infer that the group for C-t only connects to H-t. Further, H-l appears (Figs. 2B and 4C). As a result, comes Structure 6 (detailed analysis of groups a, b and resonances of hydrogen atoms on phenyl could be obtained in Ref. [18]). From the spectra we can also observe that if semibenzopinacol moieties cleaved as some literatures indicated [23–28,32] during the reaction and reacted with VAc or PVAc radicals, C-f in Structure 6 should have correlated very clearly with some other

Table 2
Results of the five comparative experiments

Experiments	Product	Soluble part (P_s)		
		Yield (mg)	M_n	PDI
1	*Before reaction*	*5.0 (S_i)*	*1900/300*	*3.43/1.21*
	After reaction	21.4	8200/400[a]	1.80/1.90
2	*Before reaction*	*5.0 (S_i)*	*1900/300*	*3.43/1.21*
	After reaction	5.0	1900/300	3.43/1.21
3	Polymer	25.4	73,900	2.25
4	No	–	–	–
5	No	–	–	–

[a] There are two peaks in the GPC spectrum.

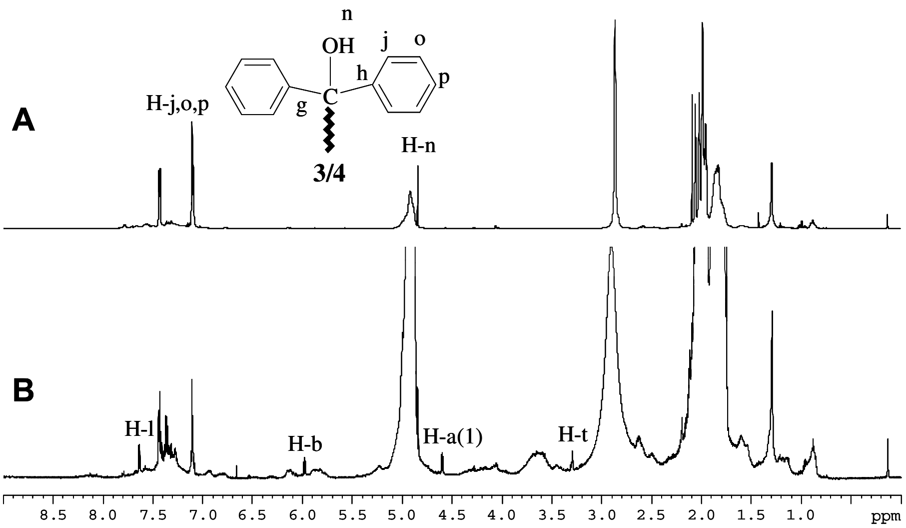


Fig. 2. 600 MHz ^{1}H spectra of S_i and its reaction products. (A) ^{1}H spectrum of S_i for Experiments 1 and 2. (B) ^{1}H spectrum of P_s from Experiment 1.

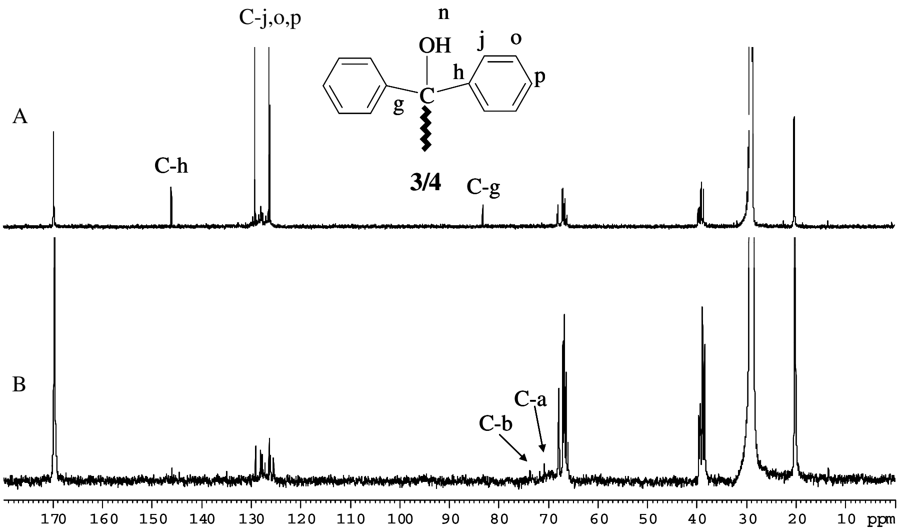


Fig. 3. 150 MHz ^{1}C spectra of S_i and its reaction products. (A) ^{1}C spectrum of S_i for Experiments 1 and 2. (B) ^{1}C spectrum of P_s from Experiment 1.

hydrogen atoms, or resonance peak of H-n (hydroxyl group) in Structure 3/4 should have interrelated with some other resonances of carbon atoms [18]. However, both these two kinds of correlations were not detected in the full HMBC spectrum, which means that most C–C bonds between C-f and another carbon atom thermally cleavable still stay intact in Experiments 1 and 2. One possible explanation is that UV light, when heating effect was removed by the condenser, could not split those C–C bonds. Instead, the hydroxyl groups under irradiation reacted to form ether.

The analyses above prove one reaction result: in the reaction system, the hydroxyl groups of semibenzopinacol moieties have reacted directly to form the new ether structure. To confirm this reaction from another aspect, the quantitative change of the resonance for H-n was then calculated together with others. Because in the process of reaction in Experiment 1 only VAc was involved besides

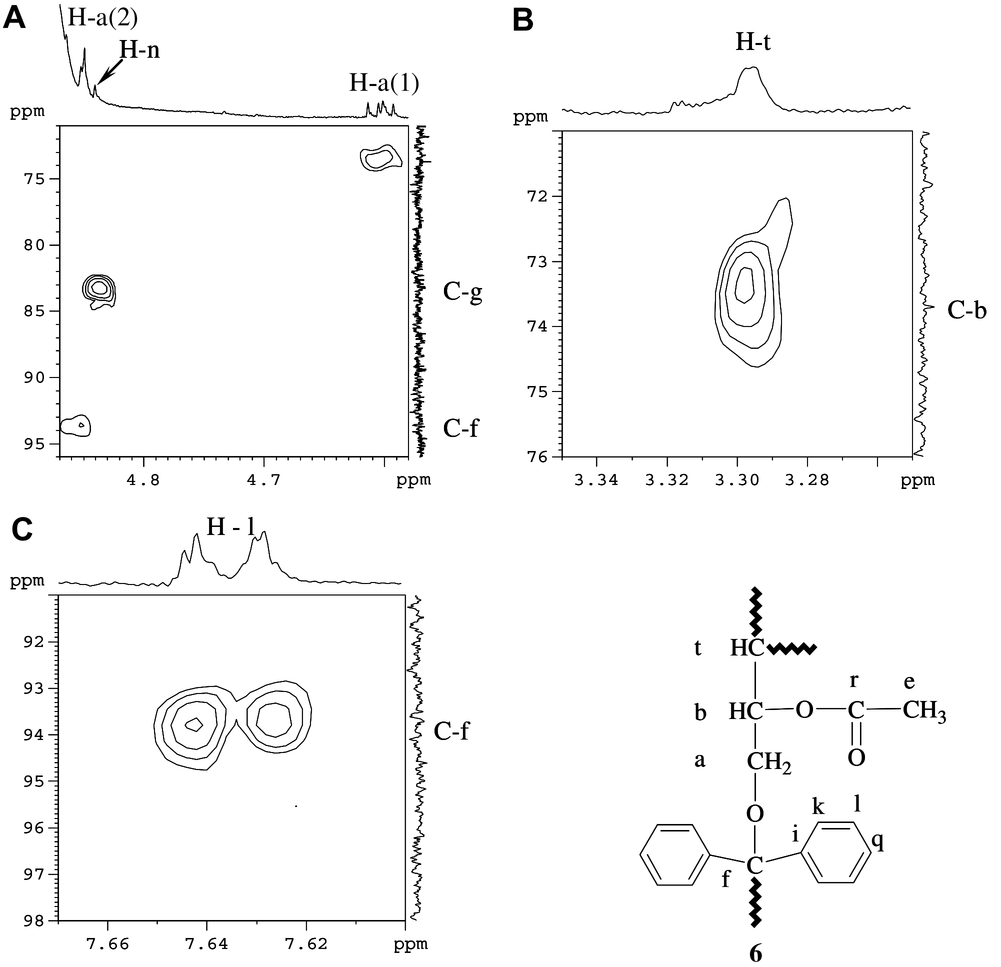


Fig. 4. 600 MHz HMBC spectra of P_s from Experiment 1 and Structure 6. (A–C) Different local HMBC spectra.

semibenzopinacol moieties and poly(vinyl acetate) components, the amount of hydrogen atoms in phenyl would not change. Before reaction, the integral ratio *I*(H-phenyl):*I*(OH)was 20.39:1.00; while after reaction, the integral ratio *I*(H-phenyl):*I*(OH): *I*(H-a(1)):*I*(H-a(2)) *I*(H-b):I (H-t) is 20.39:0.15: 0.59:0.61:0.87:0.84 (Fig. 5). There are two meanings lie in the ratios. First, Structure 6 in Fig. 4 is further supported because the integral values of H-a(1), H-a(2), H-b and H-t are very close when the deviation brought by instrument was taken into account. Second, the integral value of hydroxyl groups disappeared or reacted is 0.85 (1.00 abstracted by 0.15), close to those of H-a(2)(0.61) or H-b(0.87) appeared, which means that almost one –OH reacted to form one ether group. The explanation of the integral ratio *I*(OH) to *I*(H-phenyl) lower than 1/10 is that the acetone-d_6 used for NMR characterization is not pure but with tiny amount of D_2O, which would replace –OH into –OD and decrease the integral of –OH. However, because the volumes used for the samples before and after reaction were both 0.5 cm^3 and the low concentration of D_2O was constant, the comparison above is therefore appropriate and reliable. On the other hand, GPC analysis also revealed the reaction of hydroxyl groups to some extent. As indicated in Table 2, the molecular weights of P_s of products after Experiment 1 increased from 1900 and 300 to 8200 and 400, and the PDI changed accordingly. The most possible and apparent explanation is that the first smaller peak represents benzopinacol and the reaction of its hydroxyl group reacted to form molecules with various molecular weights and thus the PDI increased from 1.21 to 1.90, along with the increase of M_n from 300 to 400; while the larger

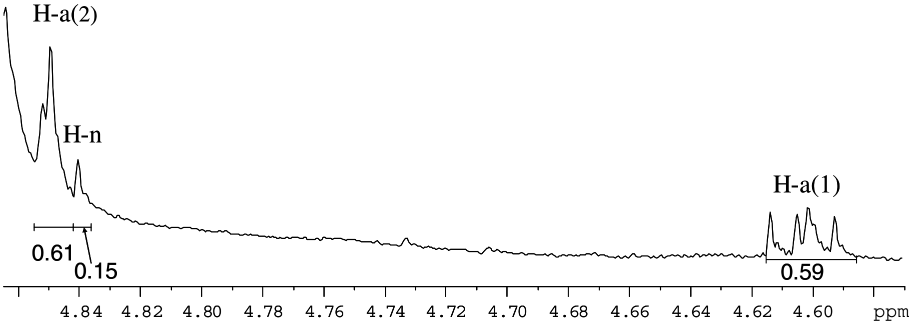


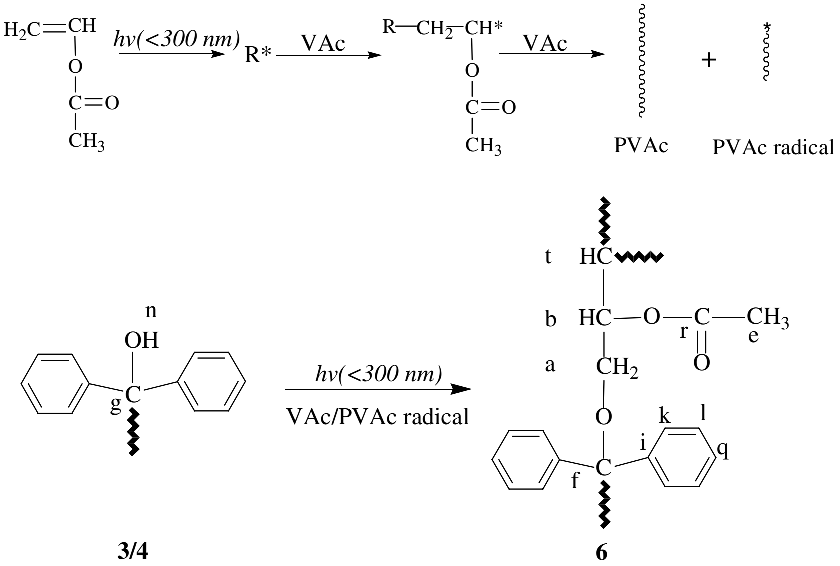
Fig. 5. 600 MHz local ^1H spectrum of P_s from Experiment 1.

peaks refers to semibenzopinacol-connected poly(vinyl acetate), which increased from 1900 to 8200 because of the reaction of semibenzopinacol moieties, and the PDI decreased from 3.43 to 1.80 because macromolecules with various molecular weights increased under similar chances and became close. In short, the reaction in Experiment 1 after taking into account of the result of Experiment 2 could be easily described as Scheme 3.

3.2. The effects of radicals and UV irradiation on the reactivity of semibenzopinacol moieties

After direct examination of the first assumption through Experiments 1 and 2, it is proved to be right and it is the reactions between semibenzopinacol moieties and other reactants, poly(vinyl acetate) radicals for example, that led to the formation of the new ether structure (Structure 1/2 or 6). Therefore, other experiments were designed in order to find out reasons for the formation of the new ether structure.

Experiment 5 demonstrated that UV light at wavelength above 300 nm could not initiate the polymerization of VAc in the reaction system as reported [33,34] or shown in the UV–vis absorption spectrum of VAc at about 223 nm in Fig. 6(a); while Experiment 4 proved that in a short time and in this reaction system, BP was not activated enough to abstract hydrogen atoms from VAc molecules and the photocycloaddition [35,36] reaction was neglectable although UV–vis spectrum of benzophenone has an absorption peak at approximately 330 nm at relatively high concentration in ethanol. On the basis of the results of these two experiments, the difference of ether formation in Experiment 1 from no



Scheme 3. A brief process presentation for the reaction in Experiment 1 (UV wavelengths < 300 nm).

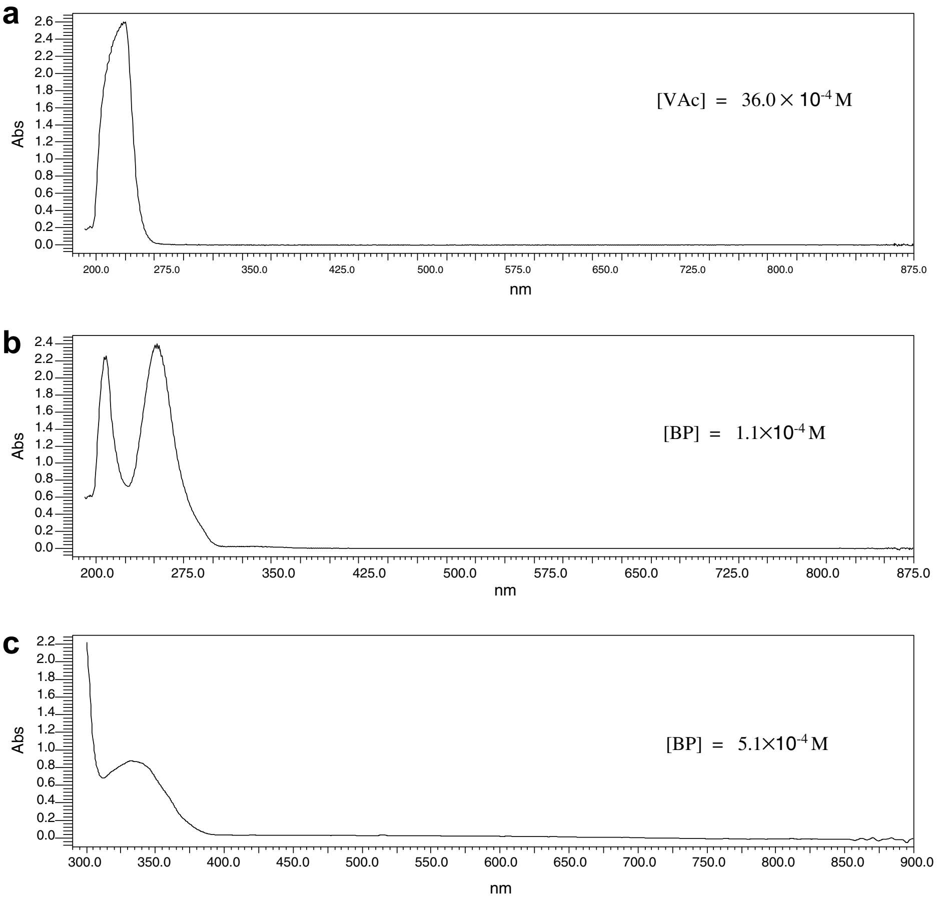
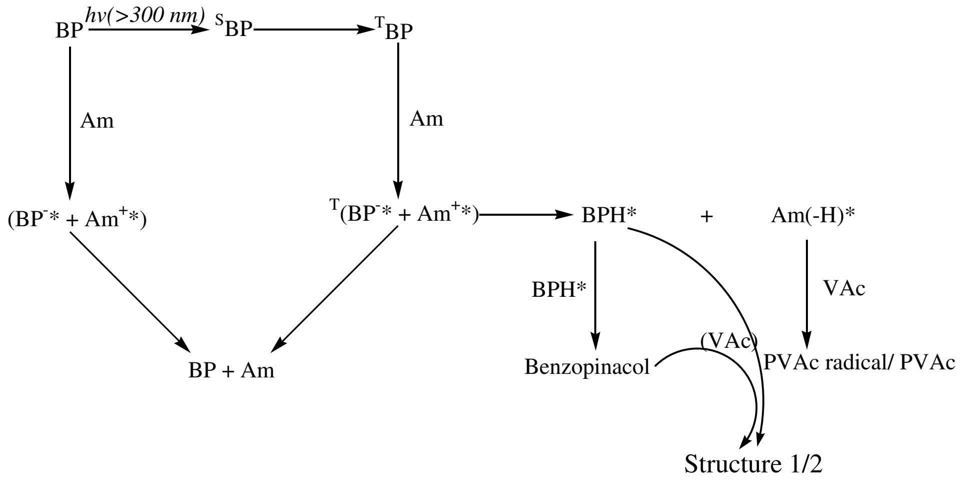


Fig. 6. UV–vis absorption spectra of vinyl acetate (a) and benzophenone (b and c) in ethanol.



Scheme 4. A mechanism of the reaction using triethanolamine and benzophenone as initiation system (UV wavelengths > 300 nm) in Experiment 3. Am: Triethanolamine.

reaction in Experiment 2 should be attributed to the PVAc radicals formed by the initiation of UV light, which means that it is the radical or the UV light under 300 nm that led to the formation of new ether

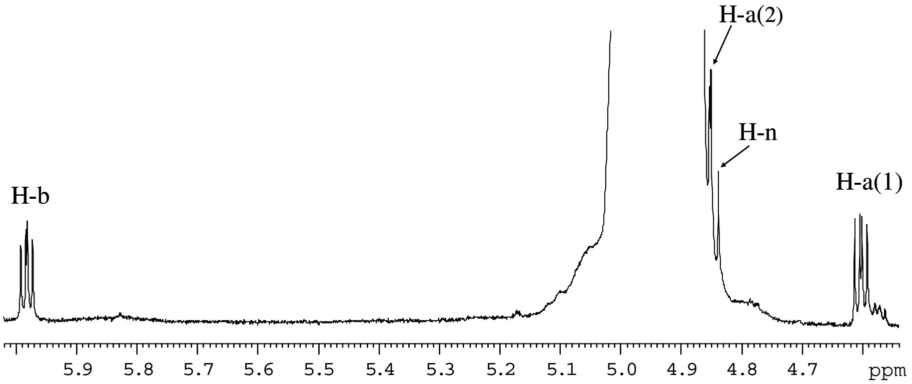
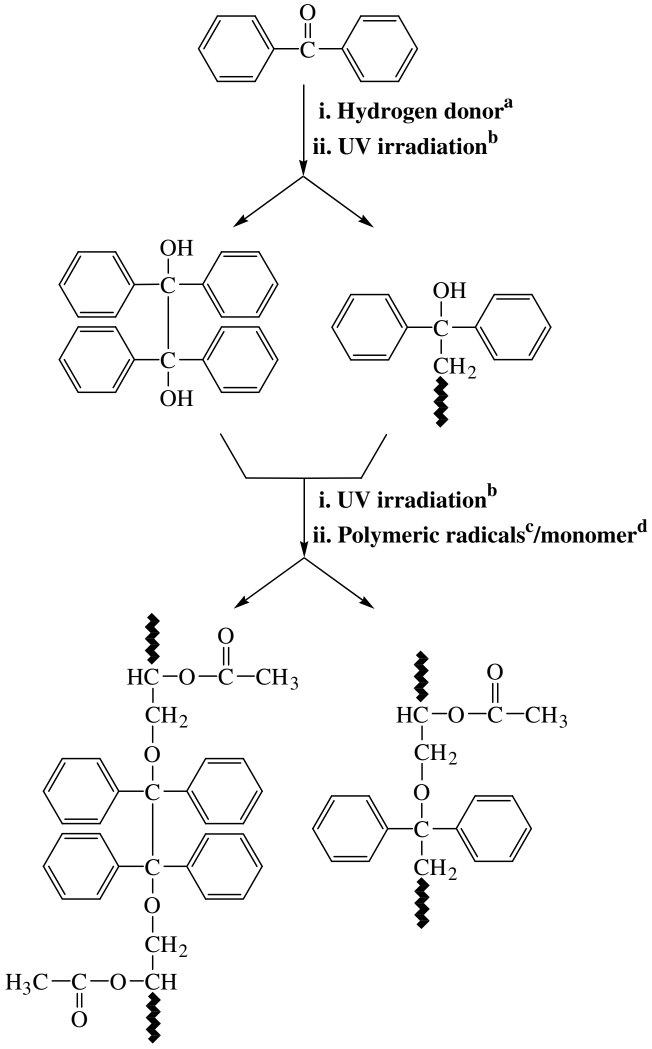


Fig. 7. 600 MHz local ^{1}H NMR spectrum of P_s from Experiment 3.



Scheme 5. A summary of the ether formation reaction. Notes: (a) vinyl acetate and poly(vinyl acetate) chain/radical; (b) UV light with wavelengths under or above 300 nm; (c) poly(vinyl acetate) radical; (d) vinyl acetate.

structure, Structure 1/2 or 6, from benzopinacol or semibenzopinacol connected poly(vinyl acetate) (the second assumption). In order to examine whether this assumption is right, Experiment 3 was especially designed.

Triethanolamine and riboflavin has been proved to be an effective photoinitiator system for vinyl polymerization in aqueous medium [33,34]. Here in Experiment 3, triethanolamine and benzophenone [35,36] were applied similarly to initiate radical reaction in the system characteristic of relatively constant intensity of absorbed UV light. The UV light was filtered by Pyrex glass to remove wavelength under 300 nm, so that whether free radicals or UV light lower than 300 nm (absorptions of benzophenone at 205 and 252 nm in Fig. 6b) responded to the direct ether formation reaction of hydroxyl group of semibenzopinacol moieties could be examined effectively. A mechanism of this initiation system for Experiment 3 is shown in Scheme 4, where benzophenone was activated from singlet state to triplet state by UV light at approximately 330 nm to abstract hydrogen atoms from better hydrogen donor-triethanolamine (Fig. 6c). After reaction and separation, P_s of the products was subjected to NMR characterization. Local ^{1}H NMR spectrum is shown in Fig. 7. Clearly the resonances for H-b, H-a(1) and H-a(2) appeared at the place exactly as mentioned before, indicating that some semibenzopinacol moieties reacted to form ether. Therefore, the hydroxyl groups are demonstrated to be able to react to generate the new ether structure even under the irradiation of UV light above 300 nm but with PVAc radicals involved. This result proved the second assumption but indicated more clearly that the hydroxyl groups of semibenzopinacol moieties were able to react to form Structure 1/2 or 6 only when there were PVAc radicals around and under UV irradiation, no matter it is above 300 nm or under 300 nm.

At this point, it is reasonable to believe that the existence of PVAc radicals initiated by UV light or by benzophenone/triethanolamine system is essential for the reaction of hydroxyl groups. At the meantime, since UV irradiation was associated with the reaction of hydroxyl group, it should have benefited the reaction because both benzophenone and semibenzopinacol moieties have absorptions of UV light under or above 300 nm [6–12,19,20]. A summary of all the results in the report could be made as Scheme 5. More detailed study on the actual wavelengths that assisted the reaction of hydroxyl is needed but this activation or absorption is one possible reason that has experimental support for the formation of the new ether structure at this time.

4. Conclusions

A reaction system characteristic of relatively constant intensity of absorbed light was designed to eliminate the heating effect and screening effect of photopolymerization. The results of five comparative experiments in this reaction system not only directly proved the reaction of hydroxyl groups on semibenzopinacol moieties to form the new ether structure but also demonstrated that the existence of PVAc radicals, whether initiated directly by UV light or through benzophenone/triethanolamine system, and UV light irradiation, whether under or above 300 nm, are two essential factors for the formation of the ether structure from hydroxyl group. While at the same time, the cleavage of the C–C bond did not happen in the examination of the reactivity of semibenzopinacol moieties, representing this cleavage must happen with actual thermal activation. The mechanism clarified here we believe should also apply to other UV-curable or photocrosslinking systems using benzophenone because those systems are somehow condensed phenomena of the hydrogen abstraction reaction of linear propagating chain here.

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