The Photosensitive Properties of Polysiloxane Acrylate Resin Containing Tertiary Amine Groups

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ABSTRACT: The photosensitive properties of a novel oligomer, di (*N*,*N*-diacrylolyl)-α, ω-diaminopolysiloxane (ANS) with tertiary amine groups and acryloyl groups in its molecular structure were investigated using FTIR and gel yield method. It was noted that the ANS system showed a notable photosensitive property and its photosensitivity in air could be up to16.3 mJ/cm^2. The UV-curing behavior of the ANS was studied by electron spin resonance (ESR). The results showed that amino-alkyl radicals can be formed by excited BP abstracting hydrogen at a-carbon bonded with nitrogen in the ANS molecule under UV irradiation, which can mitigate the oxygen inhibition in radical polymerization. It is proven that tertiary amine groups introduced into ANS could boost photosensitivity of the photopolymerization system. The oligomer ANS may find application in photopolymerization to improve the properties of UV-curing coating materials. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2944–2948, 2008

Key words: di (*N*,*N*-diacrylolyl)-α, ω-diaminopolysiloxane (ANS); photopolymerization; ESR; sensitization; spin trap

INTRODUCTION

Photosensitive silicones are widely used in various fields because of their own unique properties, such as excellent tolerance to fluctuations in temperature, good antiweatherability, low surface tension, and energy, low dielectric constant, and very resistance to ozone, environment friendly, curing at normal temperature, and energy saving.[1–5] Free radical photopolymerization silicones are paid attention, owing to rapid polymerization rate and easy adjustment in materials properties for different applications. However, a disadvantage of free radical polymerization in UV-curing process is the noticeable oxygen inhibition. To decrease the inhibition of oxygen, small molecular tertiary amine, such as triethanol amine (TEOA), was added generally, because hydrogen at α-carbon bonded with nitrogen in tertiary amine molecules can be abstracted easily to form amino-alkyl radicals, which consume a considerable amount of oxygen and ineffectual preoxide radical, leading to an effective radical generated.[6–9] Although small molecular tertiary amine could improve the photosensitivity of photosensitive system, it also brings some disadvantages of smelling, yellowing, and instability of as-prepared materials resulting in limitations to industrial applications. In recent years, the oligomers with tertiary amine groups and acryloyl groups in the molecular structure have received a wide attention, owing to decrease of oxygen inhibition without adding any extra tertiary amine.[10–12]

In this article, photosensitive properties of the UV-curable polysiloxane acrylate, di (*N*,*N*-diacrylolyl)-α, ω-diaminopolysiloxane (ANS), with tertiary amine groups and acryloyl groups in its molecular structure were investigated using FTIR and gel yield method and the UV-curing behavior of ANS was also explored by electron spin resonance (ESR). Spin trap 2-methyl-2-nitropropane (MNP) was employed to react with short-lived amino-alkyl radical to generate nitroxyl radical, adduct of the unstable radical with the trap reagent, which was stable enough for recording the ESR spectra.[13–15]

The tertiary amine groups in the ANS molecule improved the photosensitivity of the ANS system.

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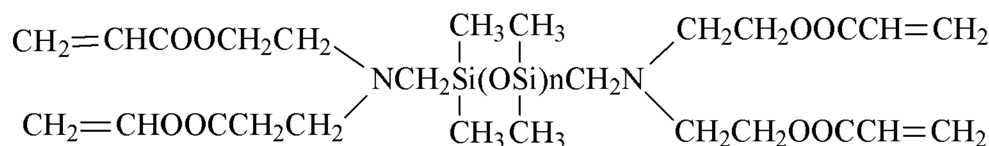
EXPERIMENTAL

Materials

The 2-methyl-2-nitropropane (MNP, AR), triethanol amine (TEOA, AR), benzophenone (BP, AR), and



Scheme 1 Molecular structure of ANS.

2,2-dimethoxy-2-phenyl acetophenone (Irgacure 651, AR) were purchased from Aldrich (USA), Beijing Yili Fine Chemical (China), Shanghai First Reagents (China), and Ciba Geigy (Switzerland), respectively, while 2-hydroxyethyl acrylate (HEA), triethylene glycol diacrylate (TEGDA), and trimethylol propane triacrylate (TMPTA) were obtained from Beijing Dongfang Chemical (China). Di (*N*,*N*-diacrylolyl)-α, ω-diaminopolysiloxane (ANS) was provided by Mendeleyev University of Chemical Technology (Russia). The molecular structure of ANS is as shown in Scheme 1.

Analysis and characterization

IR spectra were recorded on a Nicolet 50XC FTIR spectrometer (Nicolet, USA). ESR spectra were recorded at room temperature on a Bruker ESP 300E spectrometer (Bruker, USA) with 100-kHz field modulation and operating at 9.8 GHz. The samples were placed in a quartz capillary tube of 1 mm in inner diameter and scanned with the parameters of microwave power of 5 mW, modulation amplitude of 1 G, sweep time of 20 s, sweep width of 100 G, receiver gain of 5.00e + 0.04 and X-band microwave bridge.

BP and ANS were mixed with a weight ratio of 1 : 1 and subsequently dissolved into ethanol to form a stock solution with a concentration of 0.01 mol/L. About 50 μL of the as-prepared BP/ANS sample solution, 50 μL of ethanol solution of MNP (concentration of 0.1 mol/L), and 0.2 mL of ethanol were added into the quartz capillary tube and mixed uniformly by shaking. The quartz capillary tube was then placed under a high-pressure mercury lamp (500 W, wave length 320–365 nm, distance between the lamp and the quartz capillary tube was 5 cm). The solution in the quartz capillary tube was examined by ESR immediately after irradiated by UV light for a certain time, to detect the existence of amino-alkyl radical.

The photosensitivity of ANS system was determined by the gel yield method via the following procedure. Gel yield is expressed as,

$$\text{Gel yield} = W_t / W_0 \times 100\% \qquad (1)$$

where W_0 is the weight of liquid film before curing, W_t is the weight of cured film which was obtained by irradiating the liquid film under UV lamp for t seconds prior to extracting by ethanol and drying.

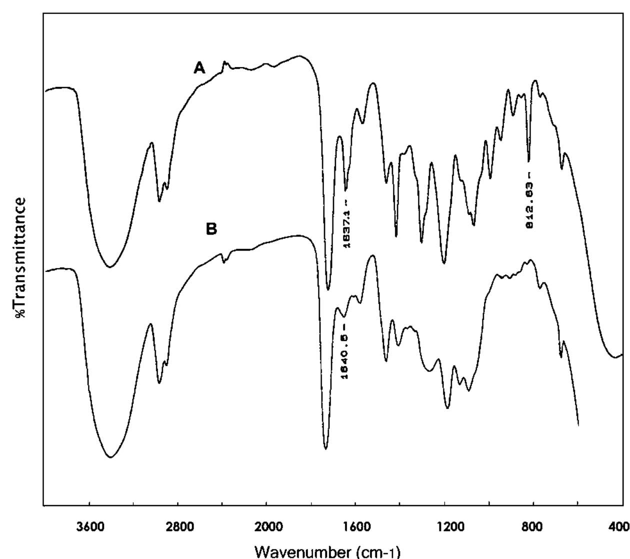


Figure 1 FTIR spectra of ANS, before curing (A) and after curing (B). Composition of the system: m (ANS) : m (Irgacure 651) = 100 : 4 (wt %).

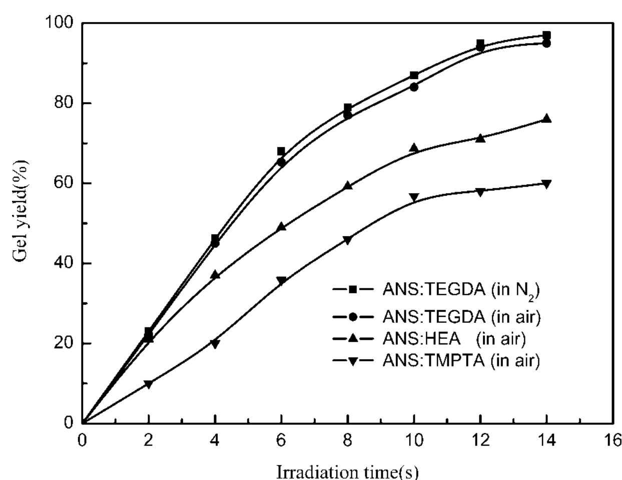


Figure 2 Photosensitive curves of the systems composed of oligomer ANS and different active monomers in air or N_2 composition of system: ANS : active monomer = 60 : 40 (wt %), m (ANS + active monomer): m (Irgacure 651) = 100 : 4 (wt %), UV curing conditions: I = 3.65 mW/cm^2, thickness of film = 74.4 μm, the distance between the high-pressure mercury lamp and the sample was 15 cm.

TABLE I
Photosensitivity of Different Photosensitive Systems in Air

Composition of the system	ANS : TEGDA	ANS : HEA	ANS : TMPTA
Photosensitivity (mJ/cm^2)	16.3	22.9	32.3

The photosensitive characteristic curve illustrates the relationship between gel yield and irradiation time. The irradiated energy responding to 50% of gel yield is evaluated as photosensitivity of the system and calculated according to the following equation,

$$\text{Photosensitivity} = I \times t\ (\text{mJ/cm}^2) \qquad (2)$$

where I is the intensity of the high-pressure mercury lamp, mW/cm^2, and t is the irradiating time when the gel yield reaches 50%, s.

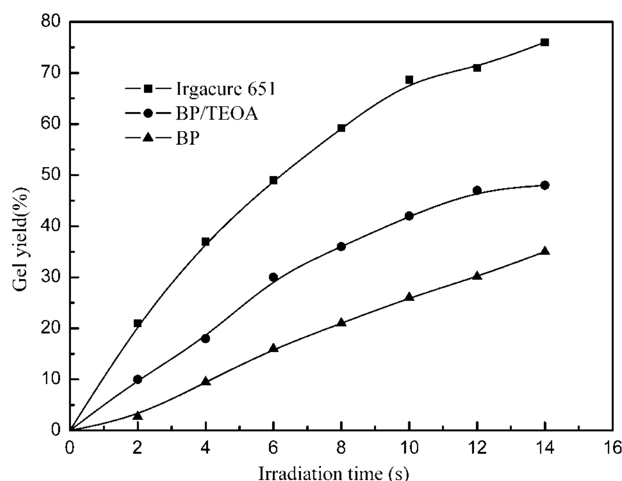


Figure 3 The effect of photoinitiator on photosensitive property of ANS system composition of system: ANS : HEA = 60 : 40 (wt %), m (ANS + HEA): m (photoinitiator) = 100 : 4 (wt %), UV curing conditions: I = 3.65 mW/cm^2, thickness of film = 74.4 μm, the distance between the high-pressure mercury lamp and the sample was 15 cm.

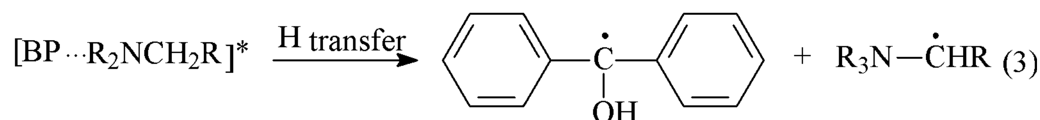
RESULTS AND DISCUSSION

Photosensitive property of ANS

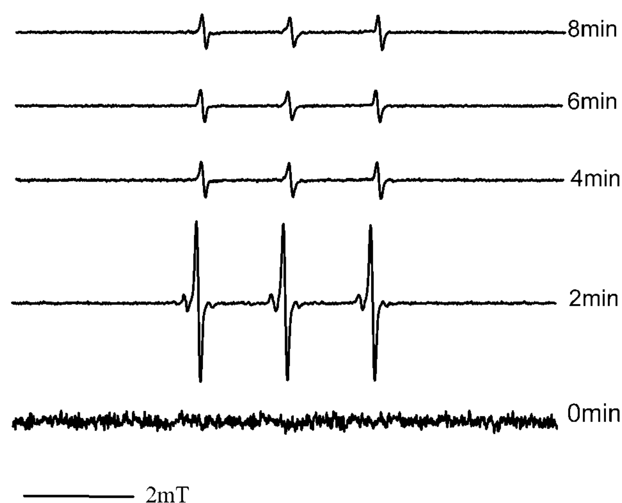
Photocuring effect was examined by FTIR as shown in Figure 1, where curve A is noncured liquid film and curve B is cured film. The absorption peaks of 1637, 812 cm^{-1} appearing in spectra A are attributed to the unsaturated C=C double bond. The absorption peaks of C=C double bond in the cured film (spectra B) decrease significantly compared with spectra A, indicating that the photopolymerization reaction of unsaturated C=C double bond occurred and ANS possesses photosensitivity.

Effect of active monomers on the photosensitive properties of ANS system

Active monomers are main component of UV curable system and play significant role on influence viscosity and photosensitive property of the system as well as physical and mechanical property of UV curable materials. Figure 2 is the photosensitive characteristic curves of the systems composed of ANS and different active monomers in air or N_2, and the photosensitivities of the systems are listed in Table I. It can be observed from Figure 2 and Table I that the photosensitivity of UV-curable system are affected by functionality and structure of monomers, and photosensitiveity of the system with TEGDA as monomer is higher reaching 16.3 mJ/cm^2 in air, which is attributed to two acryloyl groups in TEGDA molecule and good compatibility of TEGDA with ANS. Furthermore, it is observed that photopolymerization rate of ANS system in air is almost the same as that in N_2.



Scheme 2 Initiating mechanism of BP/tertiary amine under UV irradiation.



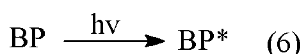
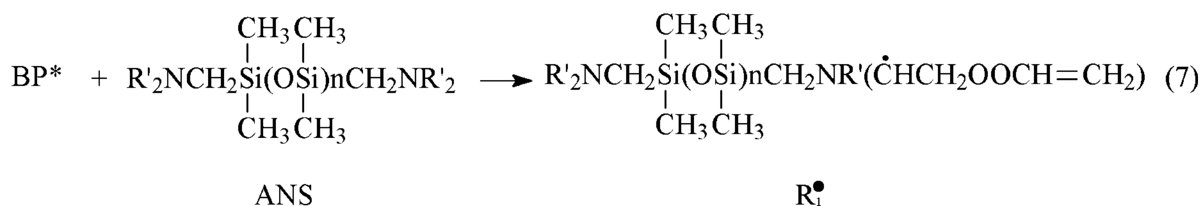


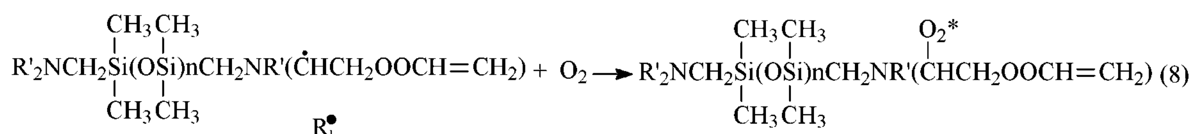
Figure 4 ESR spectra of BP/ANS/MNP system UV irradiation time: 0, 2, 4, 6, 8 min.

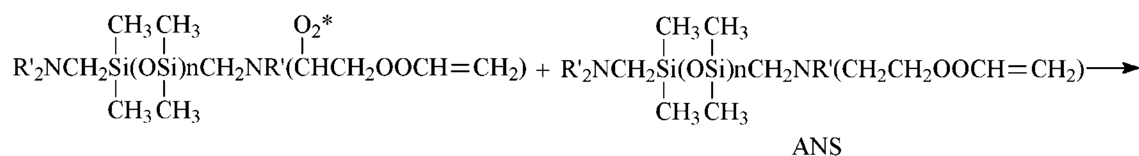
Effect of photoinitiators on the photosensitive properties of ANS system

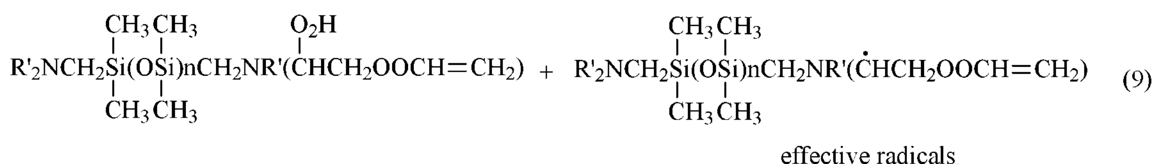
Photosensitive characteristic of UV-curing system mostly depends on photoinitiator. Photopolymerization reactions of the system composed of ANS and HEA initiated by Irgacure 651, BP/TEOA and BP were investigated, respectively. Figure 3 is the photosensitive characteristic curves of the systems composed of ANS and HEA. It is shown that photopolymerization rate of the system using Irgacure 651 as photoinitiator is faster than that using BP/TEOA or BP as photoinitiator. Irgacure 651, cleavage type photoinitiator, is photodecomposed to methyl radicals with high activity under UV irradiation, resulting in rise of photopolymerization rate. It is well know that BP is abstraction-hydrogen photoinitiator and its photoinitiation activity is to be promoted by the presence of tertiary amine as coinitiator as

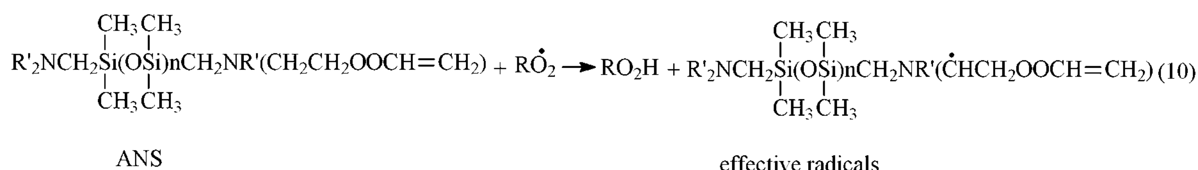


Scheme 3 The reaction of BP with ANS under UV irradiation.







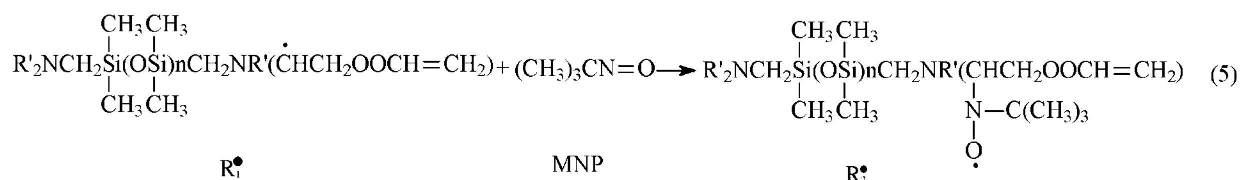


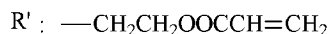
Scheme 4 The reaction of $\mathbf{R_1}$ with O_2 or preoxide radicals.

shown in Scheme 2.[6] However, it can be observed from Figure 3 that BP can initiate polymerization of the system composed of ANS and HEA without adding any extra tertiary amine, such as TEOA. It is deduced that excited BP can abstract hydrogen at α-carbon bonded with nitrogen in tertiary amine groups in ANS molecule to form amino-alkyl radical, initiating polymerization of ANS/HEA system.

UV-curing behavior of ANS

The photochemistry reaction of BP/ANS system was also explored by ESR using MNP as spin trap reagent. ESR spectra of BP/ANS/MNP system are demonstrated in Figure 4. It can be seen from Figure 4 that triplets of doublets appeared in ESR spectra when the sample were irradiated under the UV lamp for different time. The strongest ESR triplets of doublets of BP/ANS/MNP system were observed after irradiation under the UV lamp for 2 min, and the intensity of these triplets subsequently decreased with a further increase of UV irradiation time. When UV irradiation time was prolonged, free radicals coupled each other to form molecule, resulting in decrease of concentration of free radicals in the system. Triplets of doublets signal with hyperfine coupling constants $a_N = 1.60$ mT, $a_H = 0.23$ mT, in Figure 4 can be assigned to radical $\mathbf{R_2}$, spin adduct of MNP with $\mathbf{R_1}$ [see eq. (5)].[16–18]





Based on the results of photosensitive property and ESR measurements, the UV curing behaviors of ANS is proposed as follows (Scheme 3):

$\mathbf{R_1}$ can react with oxygen and ineffectual preoxide radical to generate an effective radical according to Scheme 4, leading to decrease of oxygen inhibition and improvement of photosensitivity.

The marked photosensitivity of ANS is attributed to acryloyl groups and two tertiary amine groups in the molecular structure, which can suppress the oxygen inhibition. It is proven by ESR spectra of BP/ANS/MNP (Fig. 4) that two tertiary amine groups in ANS molecule could enhance photosensitivity of the photopolymerization system.

CONCLUSIONS

Photosensitive properties of ANS systems were investigated by FTIR and gel yield method. The ANS has notable photosensitive property and photosensitivity of ANS system in air is up to 16.3 mJ/cm^2. ESR spectra confirm that amino-alkyl radical can be formed by excited BP abstracting hydrogen at α-carbon bonded with nitrogen in the ANS molecule under UV irradiation, which can mitigate the oxygen inhibition in radical polymerization. It is proven that tertiary amine groups introduced into ANS molecule could boost photosensitivity of the photopolymerization system. The oligomer ANS may find application in photopolymerization to improve the properties of UV-curing coating materials.

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