

INVESTIGATION OF UV CURING REACTION OF DICYCLOPENTADIENYL ACRYLATE BY FT-IR



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1. INTRODUCTION

Dicyclopentadienyl acrylate (DCPA) is characterized by low odor, low volatility, high flash point, low toxicity and low shrinkage on cure. Another advantage of DCPA is its insensitiveness to the inhibiting effect of oxygen. DCPA have wide industrial applications. It was used for the preparation of adhesives, UV-curable coatings and polymer concrete(1). The advantages of DCPA result from its particular structure. There are two unsaturated bonds, one acrylic double bond and one cyclic double bond, in each DCPA molecule. But, few reports on reaction behavior of the two type double bonds were issued up to date . In this paper, reaction behavior of the acrylic and the cyclic double bond of DCPA during and after UV-curing were investigated by Fourier Transform-Infrared(FT-IR).

2. EXPERIMENTAL

Materials

DCPA was synthesized by the addition of acrylic acid to dicyclopentadiene in our laboratory. Photosensitizers, Irgacure 651 and Darocur 1173, were received from Ciba Specialty Chemicals(China) Ltd.

Sample preparation

The formulation of the UV-curable sample is the following:

DCPA	100 parts
Irgacure 651	2 parts
Daracur 1173	2 parts

The sample was applied on a NaCl pellet. The exposures were carried out statically. The illumination source was a medium-pressure mercury vapor lamp,1000W/12CM.The distance between the sample and the lamp is 20 CM. The sample cured was stored in a vial with desiccant up to 82 days.

Instrument

All IR spectra were recorded by using a NICOLET AVATAR 360 FT-IR Spectrophotometer. The instrumental conditions were 32 scans and 4 CM^{-1} resolution.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Reaction behavior of DCPA unsaturated bonds during UV-curing

IR absorption spectrum of DCPA is shown in Figure 1. Two bands at 1635 CM^{-1} and 1618 CM^{-1} were found in the range of double bond absorption. They were assigned to the acrylic and the cyclic double bond, respectively.

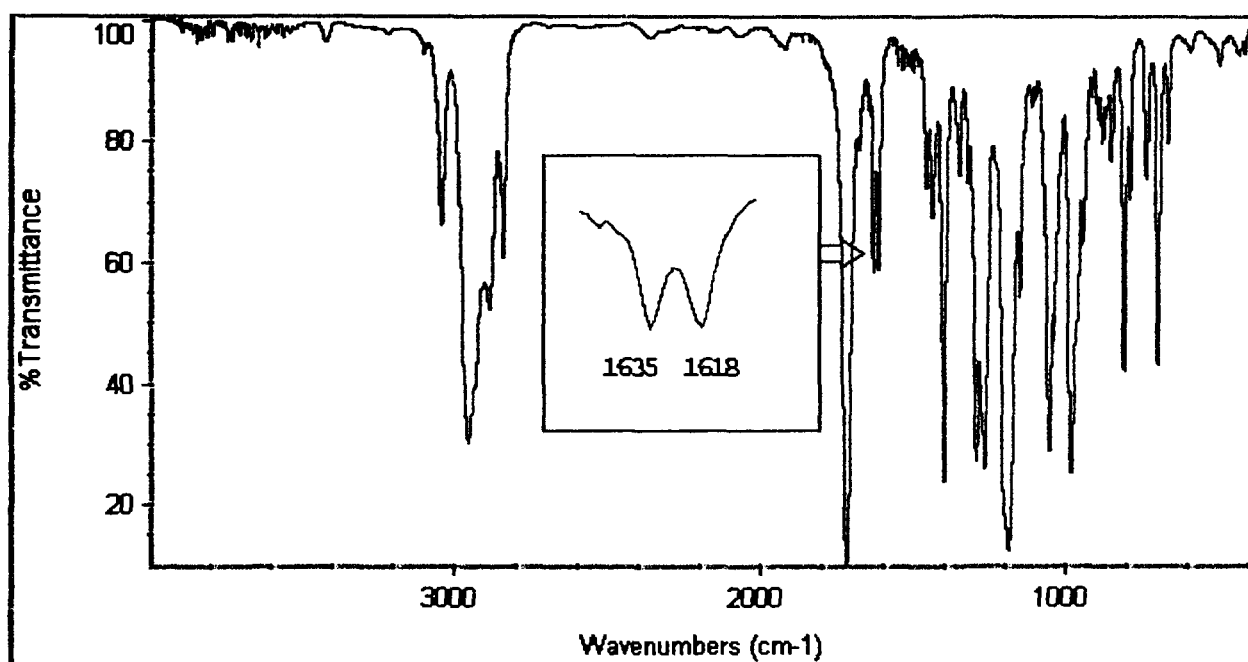


Figure 1. IR spectrum of DCPA

Figure 2 shows IR spectrum of DCPA sample illuminated with UV lamp fifteen seconds. The band of the acrylic double bond at 1635 CM^{-1} was disappeared, but the band of the cyclic double bond at 1618 CM^{-1} was no obvious change. IR spectra of DCPA sample illuminated fifteen and thirty seconds were identical. The results displays the following: (a) It is the acrylic double bond that took part in photopolymerization ; and (b) Longer time illumination couldn't initiate photopolymerization of the cyclic double bond.

Reaction behavior of DCPA cyclic double bond after UV-curing

IR spectra of DCPA sample cured were recorded on days 1, 7, 13, 18, 20, 29, 36 and 82(Figure 3 and Figure 4). While the intensity of the band at 1618 CM^{-1} decreased with the

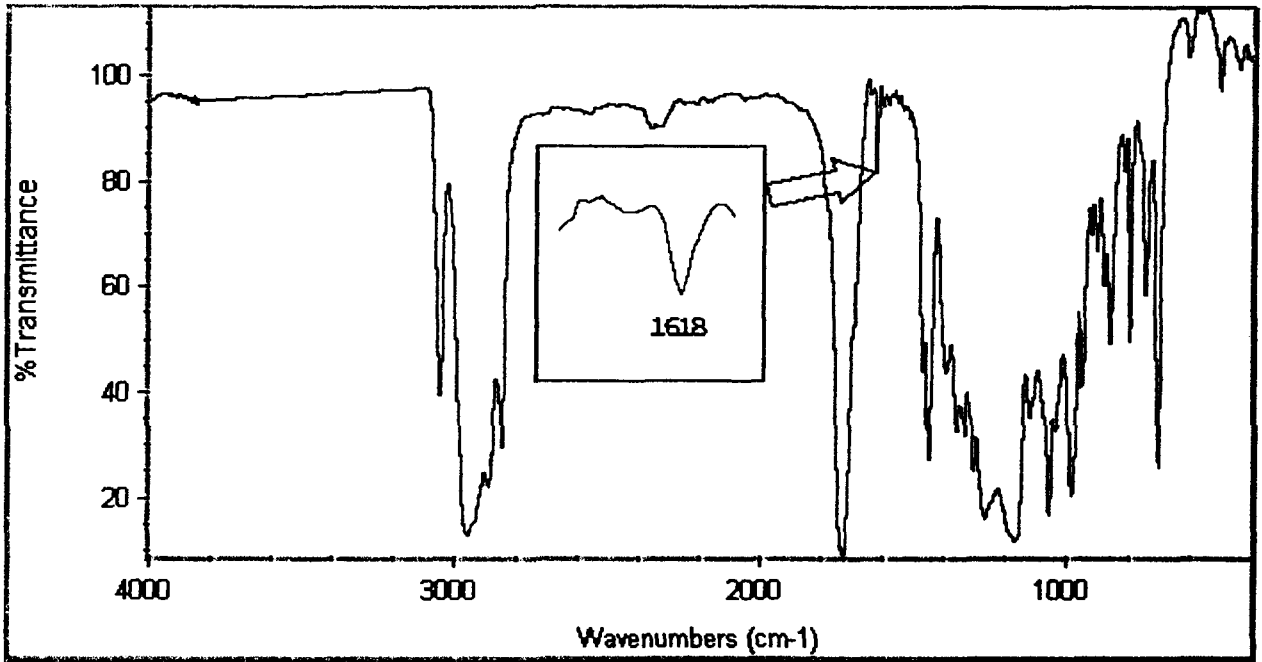


Figure 2. IR spectrum of DCPA sample cured

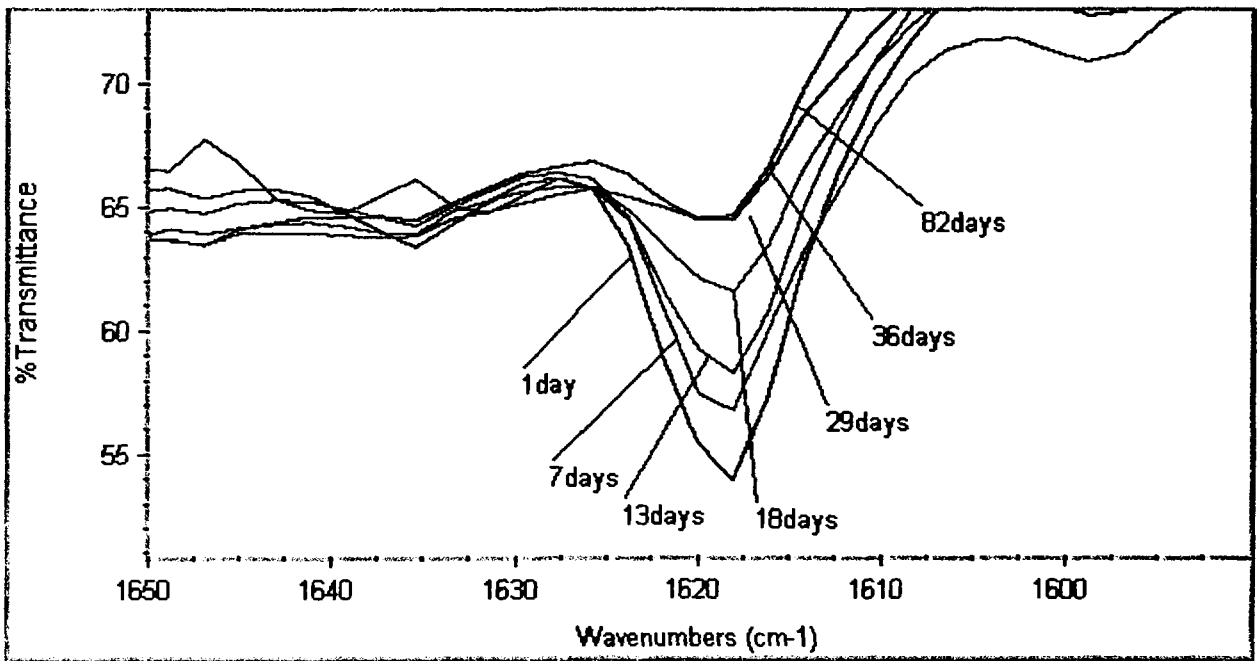


Figure 3. Time-dependence of IR spectra of the DCPA sample cured

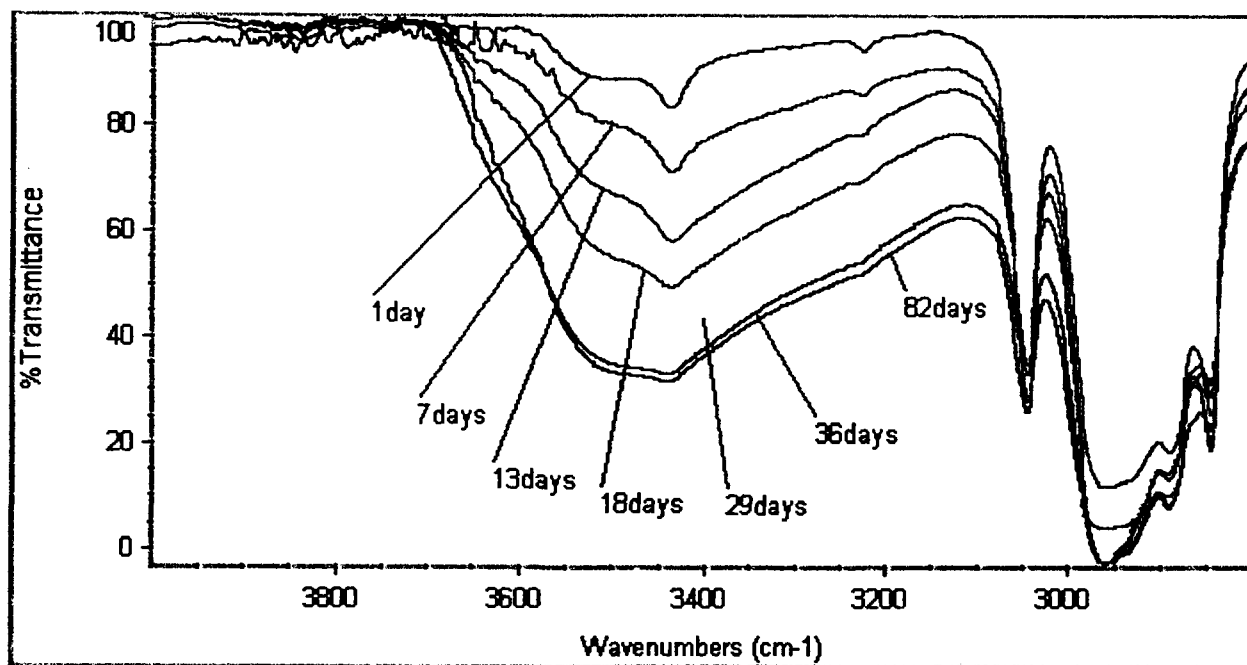


Figure 4. Time-dependence of IR spectra of the DCPA sample cured

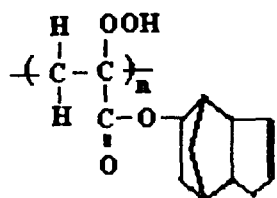
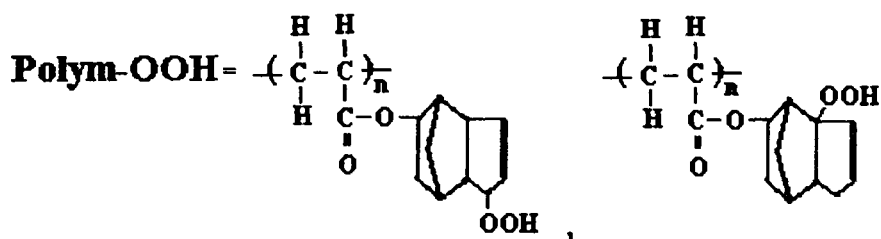
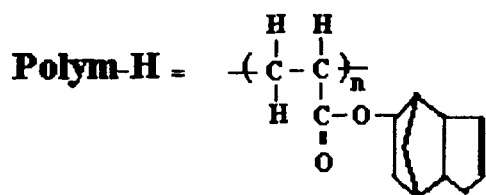
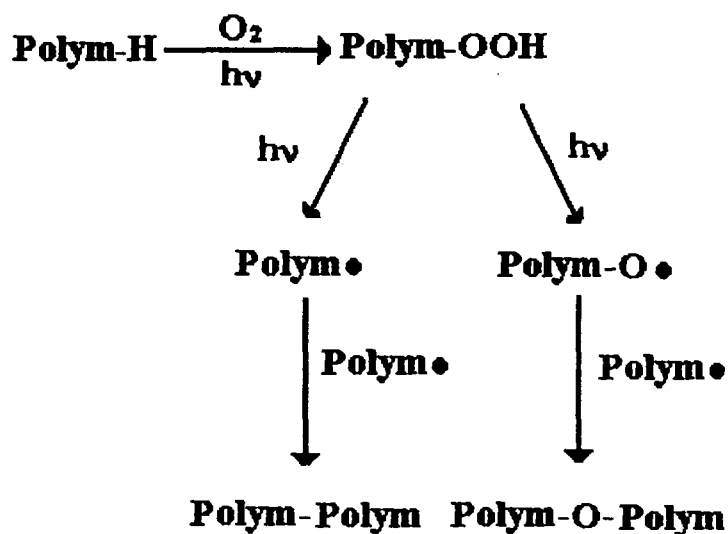
storage time over the range 1-36 days, a new wide band centered at 3400 CM^{-1} appeared and its intensity increased with time. Both of these two band intensities stopped changing after 36 days of storage. The IR spectrum didn't exhibit change on day 82 of storage as compared to day 36.

Photooxidation mechanism of DCPA cyclic double bond

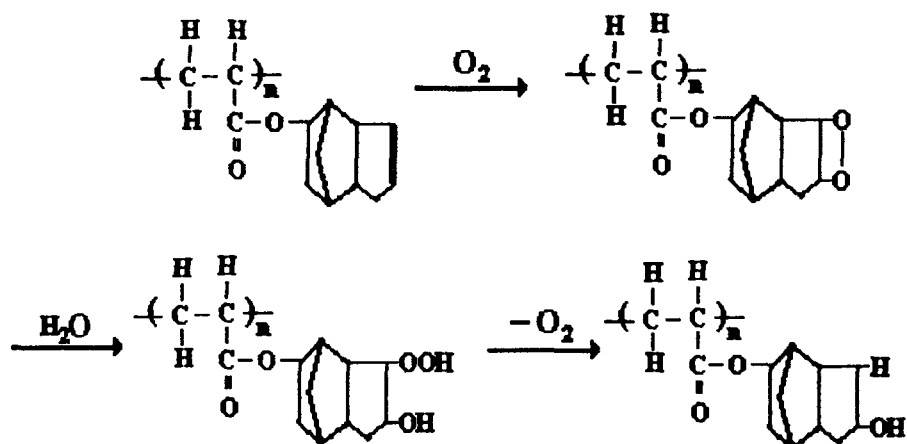
The fact that the band at 1618 CM^{-1} disappeared gradually and the band at 3400 CM^{-1} appeared indicated that the intensity variation of the band at 1618 CM^{-1} was related to that of the band at 3400 CM^{-1} and that the cyclic double bond was converted into a saturated bond, hydroxyl or hydroperoxide, by some chemical reactions.

Sisele et al(2) reported mechanism of photooxidation of DCPA homopolymer in solution (Scheme 1). If photooxidation mechanism of our experiments was consistent with Sisele's, (a) the intensity of the band of the cyclic double bond would be independent of photooxidation; and (b) the intensity of the band of hydroperoxide mid-product at 3400 CM^{-1} wouldn't increase with time. In fact, it isn't in agreement with the fact that the intensity of the band of the cyclic double bond decreased with time and the intensity of the band of hydroperoxide mid-product increased with time. Furthermore, after DCPA was cured, it is nearly impossible that hydroperoxide mid-product decomposed into free radical and initiated the cyclic double bond polymerization. It may be considered that photooxidation mechanism of DCPA after curing in our work differ from that of Sisele's in solution. The results obtained in our work can be explained in term of the proposed mechanism(Scheme 2).

First of all, DCPA cured was oxidized into a strain ring structure. It was immediately opened by an attack of a water molecule, forming a hydroxyl and a hydroperoxide. In turn, the hydroperoxide desorbed an oxygen. The final results of photooxidation were a water molecule addition to the cyclic double bond, resulting in destructing of the cyclic double bond and forming of the hydroxyl.



Scheme 1



Scheme 2

4. CONCLUSION

The polymerization of the acrylic double bond occurred during UV-curing. The remainder cyclic double bond was gradually oxidized into hydroxyl. The photooxidation stopped after 36 days. The photooxidation mechanism of forming hydroperoxide mid-product was suggested on basis of IR spectra.

Reference:

1. Eur. Pat. Appl. EP 599,7334
2. Eisele, Gilles; Fouassier; Jean-Pierre; Reeb, Roland. *Macromol. Chem. Phys.*, 1996,197(5),1731-1756