

NOTE

Radical Crosslinking in Saturated Polyesters

INTRODUCTION

The crosslinking mechanism of simple unsaturated polyesters is based on the addition of peroxides to introduce radical-induced carbon—carbon double bond opening and radical crosslinking of the resin. Such simple unsaturated polyesters are often prepared from maleic and phthalic anhydride mixtures reacting with a polyol.¹ The carbon to carbon double bond introduced in the resin skeleton by the maleic residue is the unsaturation through which radical-induced crosslinking occurs. If the polyester resin is then prepared by completely eliminating the maleic residue and basing the resin only on the reaction of phthalic anhydride with a saturated polyol, a resin incapable of radical-induced crosslinking should be produced. This,

however, does not appear to be the case, and such a “saturated” polyester resin also appears to crosslink, against expectations, through a radical mechanism, although much slower than its unsaturated counterparts. This note briefly deals with the identification of a feasible mechanism of crosslinking for such a “saturated” polyester resin.

EXPERIMENTAL

Resin Synthesis

The basic phthalic polyester resin was prepared by charging 1.05 mol propylene glycol, 1.0 mol phthalic anhydride, and 37 mg hydroquinone in a 500-mL two-necked flask equipped with thermometer, nitrogen inlet, and declining condenser fitted with a liquid trap and a gas outlet. The materials are continuously stirred under mechanical stir-

Journal of Applied Polymer Science, Vol. 43, 1585–1588 (1991)
© 1991 John Wiley & Sons, Inc. CCC 0021-8995/91/081585-04\$04.00

Table I Variation of FT-IR Bands with Advancement of the Curing Reaction of a Phthalic-only Polyester

| Band (cm ⁻¹) | Behavior | Group |
|--------------------------|--------------|--|
| 741 | Disappears | 1,2-Disubstituted aromatic from phthalic residue |
| 915 | Gets smaller | Styrene reacting; C—H stretch in RHC=CH ₂ |
| 989 | Gets smaller | Styrene reacting; C—H stretch in RHC=CH ₂ |
| 967 | Appears | 1,2,4-Trisubstituted aromatic; weak band |
| 1,061 | Appears | 1,2,4-Trisubstituted aromatic; weak band |
| 1,068 | Appears | 1,2,4-Trisubstituted aromatic; weak band |
| 1,077 | Appears | 1,2,4-Trisubstituted aromatic; weak band |
| 1,256 | Appears | |
| 1,285 | Appears | |
| 1,293 | Appears | |

| Transmission Increase and Decrease | Band Region (cm ⁻¹) | Group |
|------------------------------------|---------------------------------|--|
| Decreases | 1,645–1,640 | RHC=CH ₂ ; C=C stretch |
| Decreases | 915–905 | RHC=CH ₂ ; C—H stretch |
| Increases | 1,225–1,175 | 1,2,4-Trisubstituted aromatic and C—H in plane deformation |
| | 1,175–1,125 | |
| | 1,125–1,090 | |
| | 1,070–1,000 | |
| | 1,000–960 | |
| Increases | 860–800 | 1,2,4-Trisubstitution C—H out of plane deformation |
| | 900–860 | |

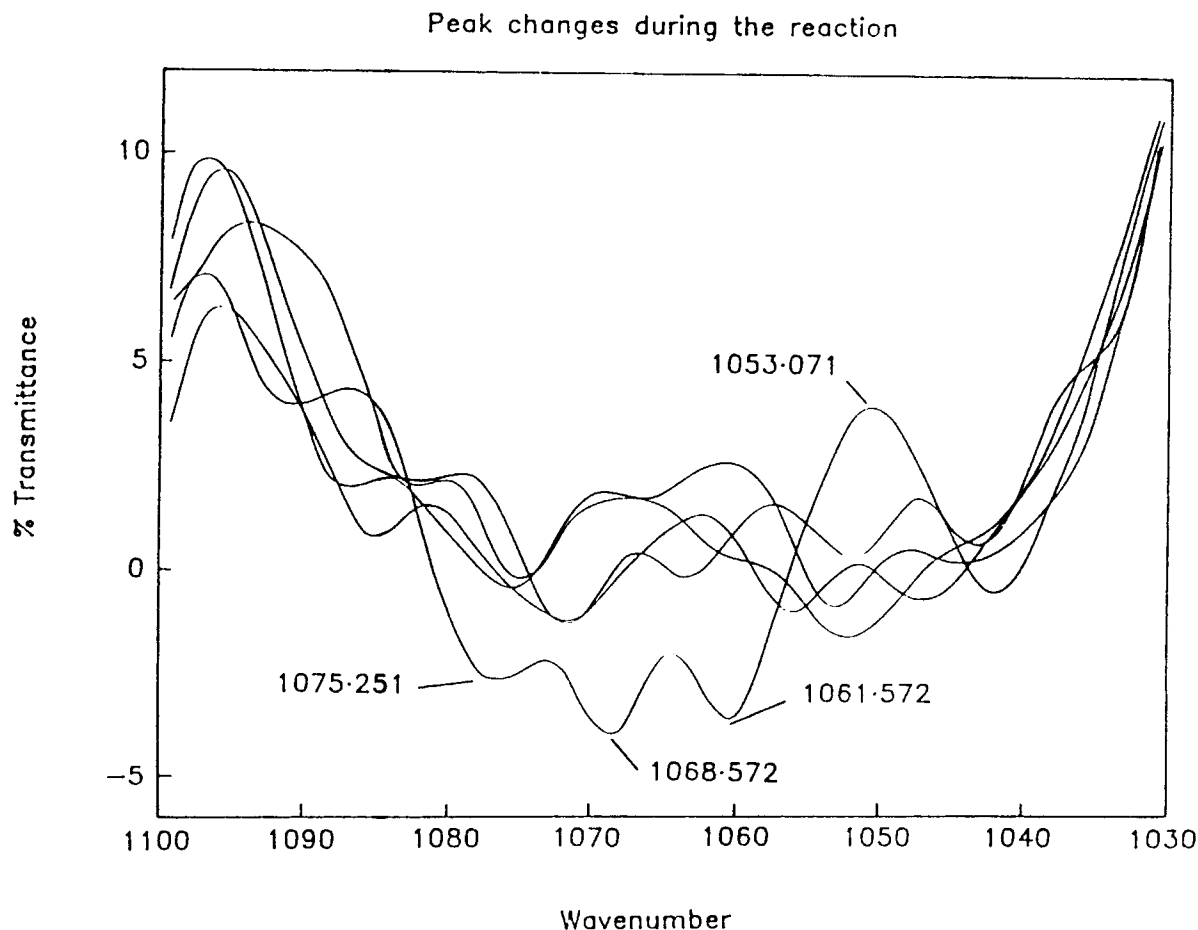


Figure 1 Variation of % transmission for 1,068 and 1,061 cm^{-1} IR bands during curing of a phthalic-based saturated polyester resin. Readings were taken at 10-min intervals. Note the start of the appearance of the two bands after 30 and 40 min and the strong bands evident after 50 min of reaction.

ring. The apparatus is then deaerated by flushing with nitrogen and then gradually heated, under continuous mechanical stirring and a slow nitrogen stream, up to 80°C. Xylene is then added to aid azeotropic distillation of the water produced in the reaction. The reaction mixture was then heated to 180°C and the temperature maintained between 180–190°C for a reaction time of 8 h, under nitrogen atmosphere and continuous mechanical stirring. The mixture was then rapidly cooled to 140°C and in one case set amounts of distilled styrene containing 0.03% hydroquinone added; in another case, the styrene was not added. The styrene, when added, was added as 10% total resin in one case and as 40% total resin in another case. A viscous clear solution of saturated polyester was obtained. Room temperature curing of the resin was carried out by adding to 100 parts by mass of resin 2 parts Co(II) naphthenate and 2 parts methyl ethyl ketone peroxide. The resins containing styrene solidified in approximately 1 h at ambient temperature. The resin that did not contain styrene increased considerably in viscosity and appeared to be almost solid after approximately 1 h.

Testing

The curing of the phthalic-based resin was followed by FT-IR. All spectra were initially collected on a JASCO 5000 FT-IR, but as a zooming facility was needed to observe the small variations in the percentage transmission of the bands involved, a Mattson Galaxy 4020 FT-IR with zooming facility was used. The uncured resin was placed as a smear between two NaCl plates. When needed, reflectance spectra and solid film spectra were also obtained on the same FT-IR apparatus. Spectra baselines were normalized for the spectra to be comparable. Scanning initially was between 4,300 and 400 cm^{-1} in percentage transmission mode. Later scanning concentrated in the 1,100 to 730 cm^{-1} range to closely follow the peaks at 1,068, 1,061, 967, and 741 cm^{-1} . In particular, the decrease in intensity of the 741 cm^{-1} indicated a decrease in the occurrence of 1,2-disubstituted phthalic residues in the skeleton of the polyester resin; and the appearance and increase of the 1,068, 1,061 and 967 cm^{-1} bands indicated

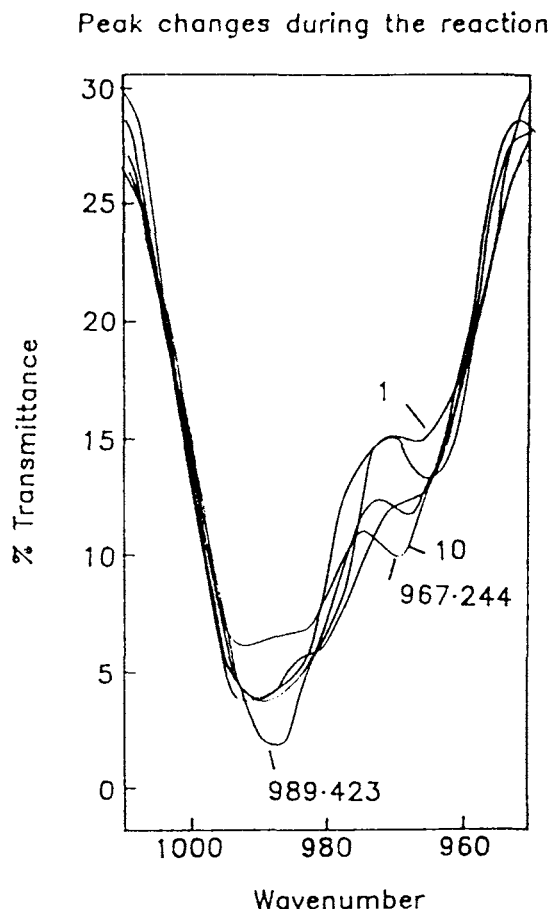


Figure 2 Appearance of the 967 cm^{-1} IR band during curing of a phthalic-based saturated polyester resin. Readings were taken at 10-min intervals. Note start of appearance of the band at 40 min and well-formed band evident after 50 min of reaction.

the appearance and increased presence of 1,2,4-trisubstituted aromatic rings. The variation of the FT-IR bands observed on curing the phthalic-based resin are shown in Table I and Figures 1-3.

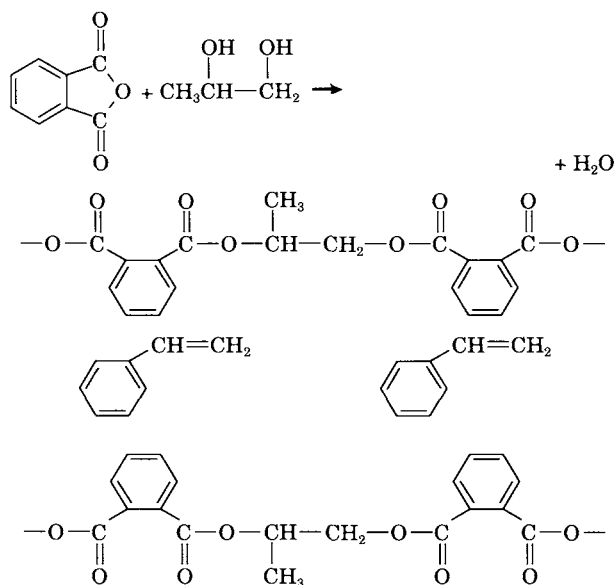
DISCUSSION

The decrease in percentage transmission of the band at 741 cm^{-1} with the advancement of resin hardening with time is shown in Figure 3. Such a decrease in percentage transmission indicates a decrease of 1,2-disubstituted aromatic nuclei from the skeleton of the polyester resin. It indicates that further substitution on the phthalic residue of the resin occurs and hence the % transmission of the characteristic band of 1,2-disubstituted aromatics is reduced. In Figure 3, the tip of the 741 cm^{-1} band eventually disappears (see curve 10, Fig. 1), but this may not mean that all the phthalic residues are not anymore 1,2-disubstituted. This is indicated by the appearance of other bands

slightly downfield, inferring that the percentage of phthalic residues that undergo further aromatic substitution may be limited. The onset of the 967 , $1,061$, and $1,068\text{ cm}^{-1}$ bands in Figures 1 and 2 indicate the progressive appearance of 1,2,4-trisubstituted aromatic nuclei. Thus, the simultaneous decrease in % transmission of the 741 cm^{-1} band and the appearance and increase in intensity of the 967 , $1,061$, and $1,068\text{ cm}^{-1}$ bands appear to indicate that some of the 1,2-disubstituted phthalic residues in the resin have reacted to form 1,2,4-trisubstituted aromatic nuclei.

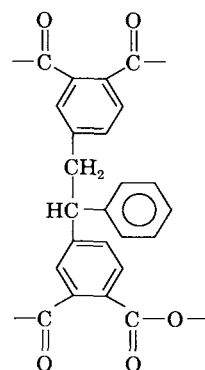
The decrease in % transmission of the carbon-carbon double bond IR band of styrene indicates that when styrene is present it is involved in the reaction in the normal manner of unsaturated polyester curing.

The simultaneous disappearance and appearance, respectively, of the 1,2-disubstituted and 1,2,4-trisubstituted aromatic bands then implies that the mechanism of crosslinking of the phthalic-only saturated polyester resin is based mainly on radical opening of styrene carbon-carbon double bonds and crosslinking of these with both themselves and with the phthalic residues in the skeleton of the saturated polyester resin. Thus:



Radical attack on double bonds

Phthalic Anhydride— 1 : 2 orthodisubstituted atom ring
— 2 Para positions reactive to attack



Formation of :

1 : 2 : 4 trisubstituted ring

$\text{CH}_2=\text{CH}-\text{R}$ disappears as styrene crosslinks

Activation of aromatic nucleus and styrene/styrene linkage

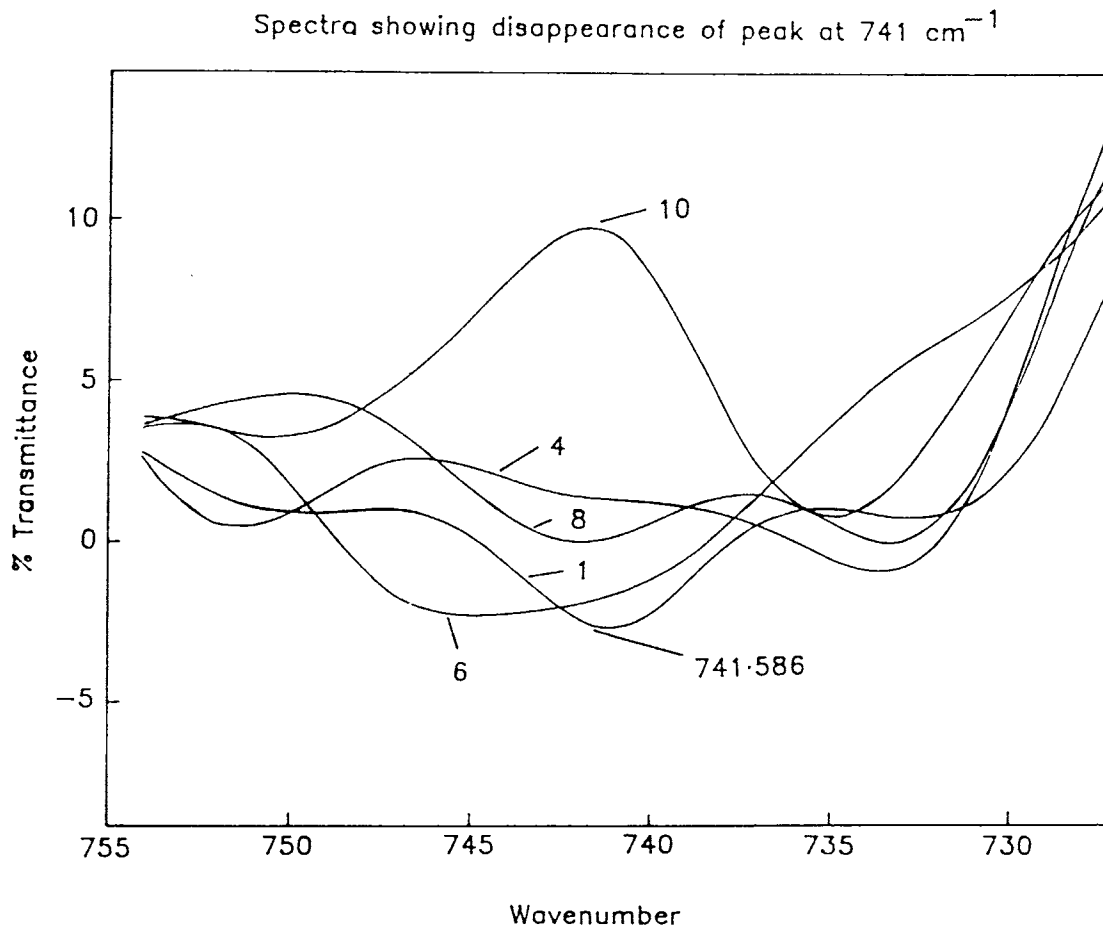


Figure 3 Disappearance of the tip of the 741 cm^{-1} IR band during curing of a phthalic-based saturated polyester resin. Readings were taken at 10-min intervals. Note the disappearance of the band after 30–40 min of reaction.

Crosslinking mechanisms other than the one proposed could also be at play, such as radical crosslinking through the C=O groups of the phthalic residues. Due to the extreme intensity of the C=O band in IR spectra, it was not possible to ascertain if such a type of crosslinking also occurs.

REFERENCES

1. M. Paauw and A. Pizzi, *J. Appl. Polym. Sci.*, **42**, 1377 (1991).

2. A. Pizzi and D. L. Watson, *J. Appl. Polym. Sci.*, to appear.

M. PAAUW
A. PIZZI

Department of Chemistry
University of the Witwatersrand
Johannesburg, South Africa

Received November 27, 1990
Accepted December 20, 1990