

## Copolymerization of diphenylmethane and *p*-xylene by oxidative coupling

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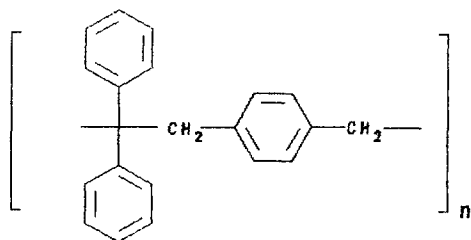
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### SUMMARY

Diphenylmethane underwent oxidative coupling in the presence of di-*t*-butyl peroxide and formed 1,1,2,2-tetraphenylethane. This coupling reaction resulted in the formation of a copolymer of diphenylmethane and *p*-xylene. The new copolymer was soluble in common organic solvents and had a molecular weight of 32,000 (polystyrene base).

### INTRODUCTION

Korshak *et al.* (1) reported that diphenylmethane (DPM) underwent oxidative coupling in the presence of di-*t*-butyl peroxide (DBPO) at 200 °C, yielding a benzene-soluble poly(diphenylmethane) which had a molecular weight of 10,000–900,000. The resulting polymer is expected to show interesting properties due to a charge-transfer interaction and/or a steric effect of the phenyl groups. However, no further study has been reported, and the formation of a DPM polymer has not been confirmed. In the present study we have reinvestigated the reaction of DPM under the presence of DBPO and deduced that DPM undergoes oxidative coupling to yield a dimer (*i.e.*, 1,1,2,2-tetraphenylethane); no further polymerization occurs due to the steric hindrance of the phenyl groups. This oxidative coupling has been applied for copolymerization of DPM with *p*-xylene and a new copolymer (I) has been obtained with a molecular weight of 32,000.



(I)

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EXPERIMENTAL

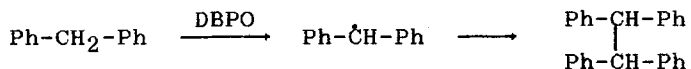
*Oxidative coupling of DPM.* A mixture of DPM (5.5 mmol) and DBPO (5.5 mmol) was heated at 200 °C for 3 h under a nitrogen atmosphere. When the reaction mixture was cooled, a colorless crystalline powder precipitated, which was recrystallized from 2-butanol and dried in vacuum. The product was characterized as the known dimer, *i.e.*, 1,1,2,2-tetraphenylethane: m.p. = 209-211 °C; mass spectrum,  $M^+$  = 334; NMR (60 MHz,  $CDCl_3$ ),  $\delta$  4.93 (s, 2, CH) and 7.26 (m, 10,  $C_6H_5$ ); the UV spectrum agreed with reported data (2).

*Copolymerization of DPM with p-xylene.* A mixture of DPM (19 mmol), *p*-xylene (16 mmol) and DBPO (21 mmol) was heated at 200-205 °C for 7 h under a nitrogen atmosphere. The resulting reaction mixture was cooled to ambient temperature, and then heated again with additional DBPO (21 mmol) at 200-205 °C for 6 h. A light yellow solid formed; it was dissolved in benzene (40 ml), and an insoluble solid, tetraphenylethane, was removed by filtration. When the filtrate was mixed with methanol (30 ml), a yellow product was obtained, which was purified from benzene and methanol. This polymer was soluble in benzene, toluene, tetrahydrofuran (THF) and chloroform. Yield: 27 %. Anal.: Calcd. for  $C_{21}H_{18}$ : C, 93.29; H, 6.71. Found: C, 92.08; H, 6.70. The elemental analyses were performed by Desert Analytics, Tucson, AZ, USA.

*Physical Measurements.* The spectroscopic data were obtained with the aid of a Perkin-Elmer 1420 IR spectrometer, a JEOL PMX-60 NMR spectrometer and a Hitachi M-80A mass spectrometer. The molecular weights of polymers were determined by the use of a gel-permeation chromatogram (GPC) composed of a Varian P2520 HPLC pump and a Perkin-Elmer Lambda 2 UV-Vis spectrometer: THF was the eluent.

RESULTS AND DISCUSSION

The reaction product of DPM in the presence of DBPO was unequivocally characterized as 1,1,2,2-tetraphenylethane. The yield of the reaction for DBPO:DPM = 1 was 12 % at 130 °C and increased linearly up to 71 % at 200 °C. The yield at 170 °C increased with DBPO:DPM ratio until the equimolar ratio. With further increase of the ratio the yield diminished. In the presence of DBPO dehydrogenation occurs at the methylene carbon of DPM to form a DPM radical, and two resulting radicals couple to form a dimer:



Under the above reaction conditions, no polymeric product was obtained. Thus, DPM underwent oxidative coupling at the methylene carbon to yield dimer in the presence of DBPO, but no further coupling occurred. Preliminary X-ray crystal analyses have been reported for 1,1,2,2-tetraphenylethane and 1,1,2,2-tetraphenylethane-1,2-diol (3). Evidently the steric effect of the phenyl groups prevents polymerization. The DPM radical, however, is expected to copolymerize with radicals that have a

smaller steric hindrance than that of DPM.

A reaction of an equimolar mixture of *p*-xylene and DPM in the presence of DBPO yielded a polymer which exhibited a single peak in the GPC. The peak maximum corresponded to a molecular weight of 32,000 (polystyrene base).

Aromatic CH out-of-plane bending bands in an IR spectrum can be used as a diagnostic test for determining the substitution patterns of phenyl groups. In this IR region, the polymer showed a band (at  $810\text{ cm}^{-1}$ ) due to a *p*-substituted phenyl group and two bands (at  $740$  and  $700\text{ cm}^{-1}$ ) due to a mono-substituted phenyl group; peaks attributable to other types of substitution were not observed (Fig. 1). Two aliphatic CH stretch bands due to a  $-\text{CH}_2-$  group were observed at  $2920$  and  $2860\text{ cm}^{-1}$ ; a band attributable to  $\text{CH}_3-$  group was not appreciable. This IR spectrum, together with the observation of a single GPC peak, is evidence for the formation of the copolymer (I), in which DPM and *p*-xylene are linked with each other at their aliphatic carbons. The peak-height ratios of the CH out-of-plane bending bands are approximately equal to those observed for an equimolar mixture of DPM and *p*-xylene. Therefore, the ratio of the two monomers in a polymer is:  $[\text{DPM}]/[\text{xylene}] \approx 1$ . This is consistent with the CH-analysis data.

The  $^1\text{H}$  NMR spectrum of the  $\text{CDCl}_3$  solution showed an aromatic proton peak at  $\delta = 7.2$  ppm and a methylene proton peak at  $\delta = 2.3$  ppm. The ratio of the integrated intensities of the two peaks was:  $I(2.3):I(7.2) \approx 1:6$ , from which the monomer content ratio in the copolymer was calculated as  $[\text{DPM}]/[\text{xylene}] \approx 1.5$ . This NMR result shows that the concentration of xylene units is not larger than that of DPM units, although the integrated intensities have large uncertainties due to the very large peak widths.

The large steric effect in DPM makes it difficult to form a  $-\text{DPM}-\text{DPM}-$  unit. A DPM unit is, therefore, bonded to two xylene units on either side; DPM and xylene are expected to be linked in an alternating manner.

A reaction for xylene:DPM = 2:1 provided a copolymer, which had a molecular weight of 32,000. The IR and NMR spectra were practically identical with those of the product obtained for xylene:DPM = 1:1. The composition of the product is independent of the monomer ratio employed in the polymerization reaction.

When *p*-xylene was treated with DBPO under the same condition as for the copolymer without mixing with DPM, a light yellow

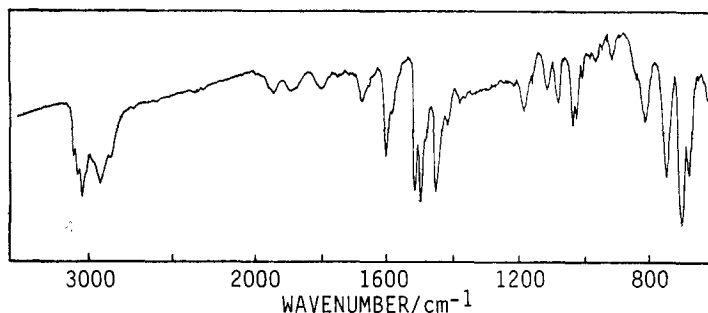


Fig. 1. IR spectra of diphenylmethane-xylene copolymer.

polymer was obtained. Since this polymer was insoluble in common organic solvents, further characterization was difficult. It is evident, however, that *p*-xylene undergoes oxidative coupling in the presence of DBPO.

In conclusion, a reaction of DPM and *p*-xylene in the presence of DBPO forms a new copolymer (I), in which DPM and *p*-xylene units are probably linked in an alternating manner.

#### ACKNOWLEDGEMENTS

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