^{13}C NMR Study on the Reaction Product of Maleic Anhydride and Poly(2,6-dimethylphenylene ether)

J. H. Glans* and M. K. Akkapeddi

Engineered Materials Sector, Allied Signal Inc., Columbia Road, Morristown, New Jersey 07962

Received May 17, 1990; Revised Manuscript Received August 14, 1990

ABSTRACT: The mechanism of the reaction of maleic anhydride with poly(2,6-dimethylphenylene ether) (PPE) was investigated by ^{13}C NMR spectroscopy of PPE samples reacted with ^{13}C-labeled maleic anhydride. There are several sites of attachment to the PPE backbone and chain ends. The proportions of each are dependent on the prior treatment of the polymer sample. Several possible structures for these adducts are presented.

Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE, also commonly referred to as poly(2,6-dimethyl-1,4-phenylene oxide or PPO) is a well-known polymer[1] with a unique combination of useful properties such as a high glass transition temperature (205 °C), dimensional stability, and intrinsic ductility. However, because of its high melt viscosity, requiring high processing temperatures, and a tendency for thermooxidative degradation in the melt, pure PPE could not be used as an injection molding, engineering resin.[2] So far, the largest commercial usage of PPE has been in a family of engineering resin blends based primarily on impact-modified polystyrenes. Since PPE was found to be thermodynamically miscible with polystyrene,[3] blends offering a wide range of properties and processability could be readily produced.

Although it is desirable to blend PPE with other common thermoplastics such as polyamides, polyesters, etc., immiscibility or incompatibility between the polymers leads to poor interfacial adhesion and hence brittleness in the blends. In principle, compatibilization of immiscible polymer blends can be improved through the incorporation of block or graft copolymers.[4] Such graft copolymers can be generated in situ in the blend via a reactive extrusion process, provided the individual polymers contain suitable reactive functionalities either as end groups or as a modification on the backbone.

Modification of a hydrocarbon polymer backbone such as polyolefin by postreaction with maleic anhydride ("maleation") via thermal and radical initiation has been known for some time.[5] It is also known that alkylbenzenes undergo addition reactions with maleic anhydride.[6] Hence we postulated that PPE could also be functionalized by some type of addition reaction with maleic anhydride and other such unsaturated compounds. Except for some patent literature,[7] very little is known about the chemistry of maleation of PPE or the subsequent grafting of this species to other thermoplastics. This patent literature primarily dealt with the preparation of PPE–polyamide blends compatibilized by maleic anhydride and was presumed to involve grafting reactions. The objective of our study was to elucidate the mechanism of maleation of PPE via structural investigation of the adduct by NMR. In order to enable us to see the relatively weak resonances of the grafted anhydride moiety in the ^{13}C NMR, we have used ^{13}C-labeled maleic anhydride in our studies. In this paper we report some of the results of our investigation.

Chart I

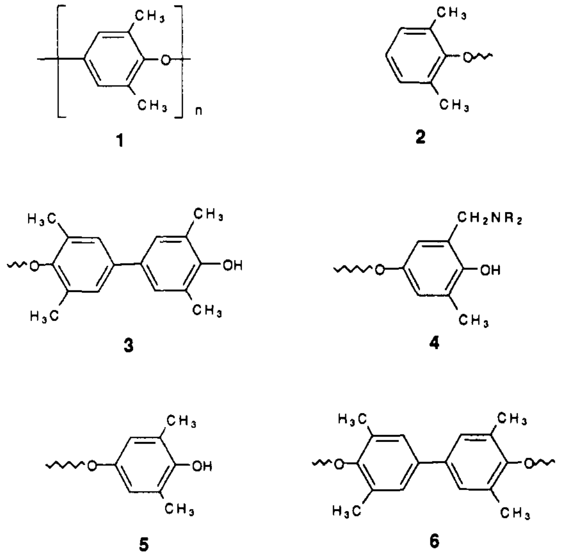


Table I
Amine Content of Several PPE Samples Prior to Maleation

sample	treatment	amine, mequiv/g
I	none	0.194
II	pptd	0.283
III	vac strip	0.065

Experimental Section

Poly(phenylene ether) (PPE) with an intrinsic viscosity of 0.45 dL/g ($CHCl_3$) and a phenolic hydroxyl content of 0.07 mequiv/g was used. The phenolic end group concentration was determined by potentiometric titration with tetra-*n*-butylammonium hydroxide in a manner similar to the procedure used in the literature.[8] Maleic anhydride labeled with ^{13}C on the olefinic carbons was used as received from Merck Isotopes (St. Louis, MO). ^{13}C NMR spectra were obtained on a Varian XL-400 spectrometer at 100 MHz in 10-mm-o.d. tubes at 30 °C. The ^{13}C double quantum filtered COSY experiment was run using standard Varian software (version 6.1). A total of 450 t_1 increments with acquisition times of 0.043 s was used. The resulting 2048 × 450 data matrix was zero filled in t_1 to 2048 × 2048 data points and Fourier transformed with a pseudoecho weighting function applied in both dimensions. Amine titrations were conducted potentiometrically in chloroform/trifluoroethanol (30:5) and titrated with *p*-toluenesulfonic acid in trifluoroethanol in a manner similar to the procedure normally used for determining amine end groups in nylons.[9]

A sample of the PPE was vacuum stripped by extrusion on a Killion single-screw extruder (30:1) fitted with a vacuum port.

Maleation of PPE with ^{13}C-Labeled Maleic Anhydride. A mixture of PPE (1.0 g) and labeled maleic anhydride (0.1 g) was

0024-9297/91/2224-0383$02.50/0

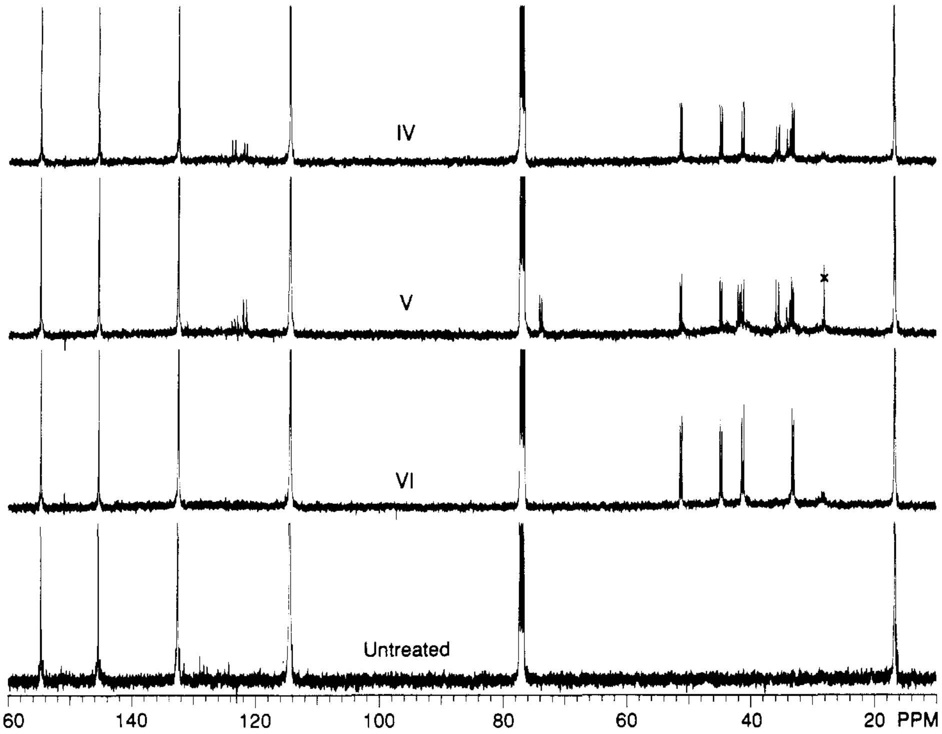


Figure 1. ^{13}C NMR spectra of maleated PPE samples.

added to a thick-walled polymerization tube. The tube was vacuum purged with argon 3 times. Filled tubes were placed in a heating block at 280 °C for 1.8 h. The tubes were allowed to cool and broken open. The residue was dissolved in chloroform and precipitated into methanol. The resulting tan powder was dried under vacuum at 110 °C overnight.

Results and Discussion

PPE is formed by the oxidative polymerization of 2,6-dimethylphenol with oxygen in the presence of a copper salt and an amine cocatalyst. The structure of the polymer backbone and the end groups of PPE have been well characterized by ^{13}C NMR;[10] these units, 1–4, are shown in Chart I, with structures **5** and **6** being present in smaller quantities. It is interesting to note that a majority of the polymer chains have incorporated some of the amine cocatalyst as a (dialkylamino)methyl group on the phenolic terminus of the chain. During maleation it is expected that the maleic anhydride will react with one or more of the groups shown in Chart I.

A sample of the commercial resin was vacuum stripped in the melt phase at 280 °C on a single-screw extruder to remove any terminal amine groups. Another sample was precipitated into methanol from chloroform to remove any residual catalysts. Table I shows the amine levels in these samples as determined by titration. It is interesting that the amine content of the PPE increased upon precipitation. It was anticipated that this step would remove any unbound amine present. The precipitation step may have removed low molecular weight materials, giving an apparent increase in amine content.

Table II
Anhydride Content of Maleated PPE Samples

sample	PPE sample	anhydride, mequiv/g
IV	I	0.22
V	II	0.17
VI	III	0.28

Table III
^{13}C NMR Data for Maleated PPE

			multiplicity[a]		
peak	shift, ppm	$^{1}J_{CC}$, Hz	$^{1}J_{CH}$	$^{2,3}J_{CH}$	structure
1	123.7	48.3	s	t	A
2	121.8	48.3	s	t	B
3	74.0	36.3	d		C
4	51.3	32.5	d	s, d[b]	D
5	44.8	32.2	d	t	D
6	41.9	35.9	d		C
7	41.3	34.6	d	m	E
8	35.6	49.0	t	d	A
9	33.9	48.4	t	d	B
10	33.2	34.8	t	m	E

[a] s = singlet, d = doublet, t = triplet, m = multiplet. [b] One branch was further split into doublets and the other was not.

Samples were maleated as detailed in the Experimental Section. Dried samples were analyzed by high-field ^{13}C NMR. Figure 1 shows the proton-decoupled ^{13}C NMR spectra for each of these samples compared to unmodified PPE. Table II shows the level of anhydride incorporation for each sample as determined by integration of the NMR spectra. It should be noted that these values are only approximate as a quantitative NMR experiment was not done. Table III lists the chemical shift data assignable to five different types of structures (A–E). The multiplicities of the one-, two-, and three-bond carbon–hydrogen couplings were determined from a proton-coupled spectrum of V. Each of the samples showed different combinations of these structures.

The maleic anhydride used in this study was labeled with carbon-13 at both of the olefinic carbons. Grafted structures that are unsymmetrical will therefore show two peaks in the ^{13}C NMR. These peaks will appear as doublets due to the C–C coupling of this nucleus. Coupling constants are a good guide for pairing up the peaks associated with any given structure. This was confirmed by a 2D NMR cross correlation experiment (Figure 2). The last column in Table III shows which peaks are paired. None of the samples show any residual maleic anhydride. There are also no simple olefins present, eliminating reaction at non-olefinic sites. The sample that was precipitated (V) had all of the structures shown. The unmodified sample (IV) had all of the structures except C.

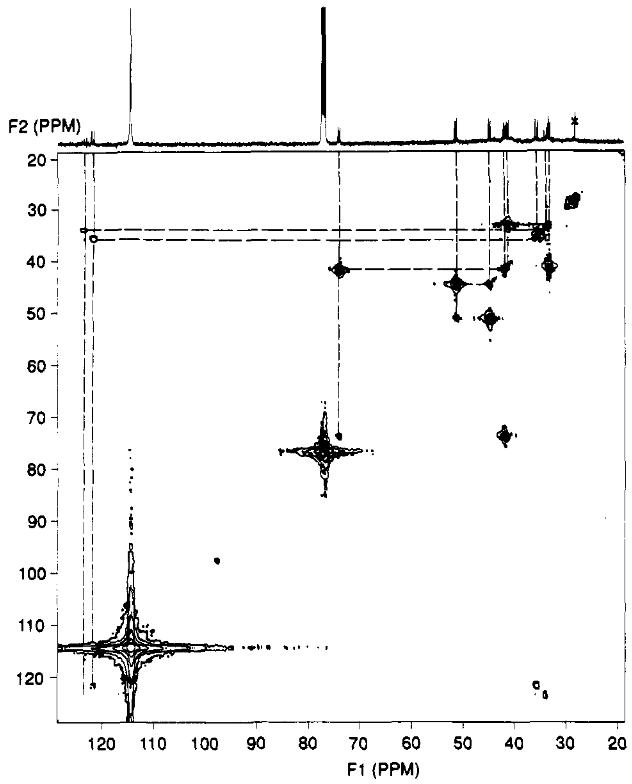
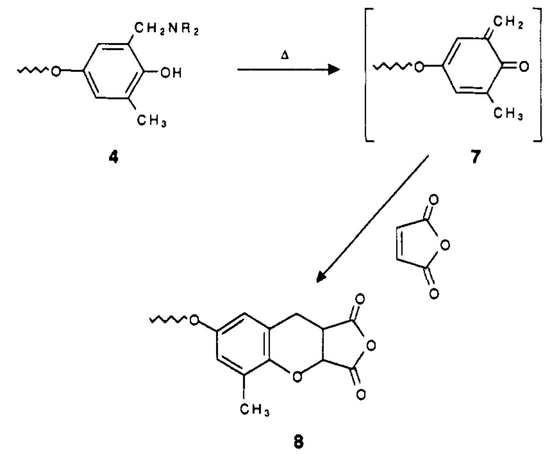


Figure 2. ^{13}C COSY spectrum of maleated PPE V (only a portion of the spectrum is shown for clarity).

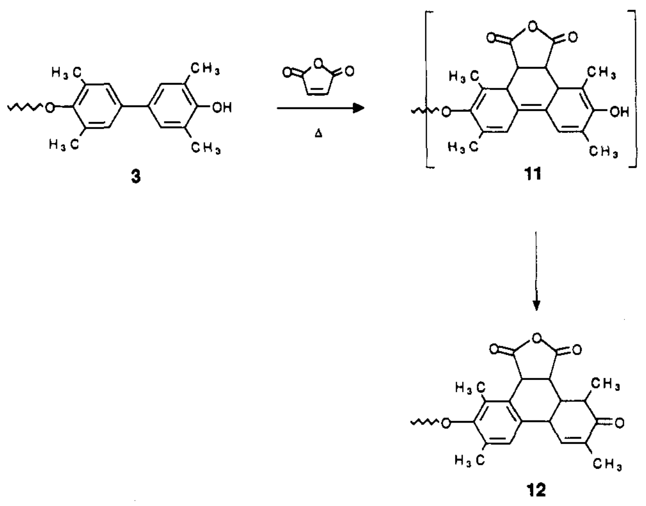
Scheme I



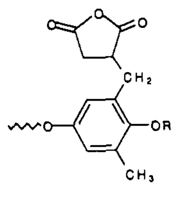
The vacuum-stripped sample (VI) had only structures D and E. A sample of IV was examined before precipitation and found to have the same spectrum as that of the precipitated sample, showing that no unbound species are being formed. Also, a sample of IV was extracted overnight with acetone to remove any unbound structures that might have been left after precipitation; however, no change was seen in the spectrum.

Structure C is only seen in the precipitated sample, which also had the highest nitrogen content. From the NMR this structure is disubstituted with one bond to a carbon and one to an oxygen. This structure is likely due to the adduct of the anhydride with the *o*-quinomethide intermediate (8) (Scheme I). This structure is not expected to be an important route to maleation as preextruded samples that no longer have the dialkylamino end group 4 show comparable levels of maleation to those of untreated PPE.[11] This is confirmed by the fact that none of this structure is seen in sample VI.

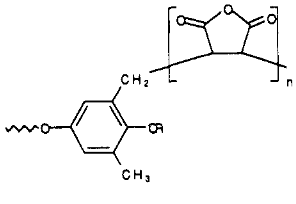
Scheme II



Structure E appears to be a monosubstituted adduct with an adjacent methylene group. This adduct is most likely due to addition of the olefin into a carbon–hydrogen bond on one of the methyl groups (9). This structure may be formed by reaction of the anhydride with a benzylic radical.



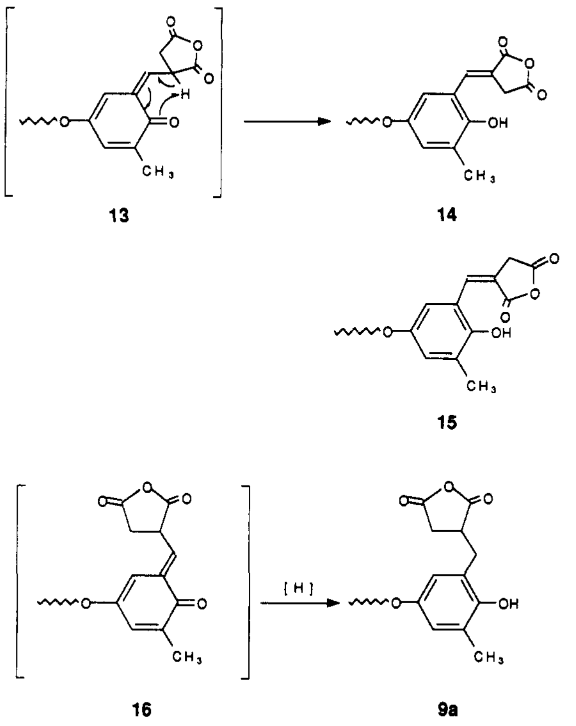
9a, R = H
b, R = ∿∿



10a, R = H
b, R = ∿∿

Structure D is disubstituted with carbons attached to both labeled carbons. One possibility would be a poly(maleic anhydride) adduct attached to the polymer backbone (10). Poly(maleic anhydride) is known[12] and has been reported to have a chemical shift of 44.8 ppm. If this structure was present C–C spin multiplicities of greater than 2 would be seen; as this is not so, this structure must be eliminated. From the $^{2}J_{CH}$ splitting data one of the carbons adjacent to the anhydride ring has a single proton and the other no protons. A possible structure is the Diels–Alder adduct of the anhydride with biphenyl chain ends (12) (Scheme II). Although some aromaticity is lost in this structure, the final product should be nearly as stable as the starting ether phenol (3). An interesting feature of this structure's spectrum is the difference in $^{2}J_{CH}$ couplings in the two branches of the line for the downfield carbon. One branch is unsplit by neighboring protons, and the other is split into a doublet. We have no explanation for this phenomenon.

Structures A and B are similar and have one olefinic carbon and one aliphatic carbon. The aliphatic carbon has two attached protons and the olefinic carbon none. Long-range C–H coupling (two and three bond) shows that there are two protons on carbons adjacent to the olefinic carbon and one adjacent to the aliphatic. It is likely that these structures are isomers due to their similarities. One possibility would be isomers 14 and 15 (Scheme III). These could arise from a rearrangement of the substituted *o*-quinomethide intermediate 13. It is difficult to hypothesize how intermediate 13 would form without more information. One possibility for structure E would be **9a**, Scheme III



13 14 15 16 9a

arising from the reduction of the other isomer of intermediate 13 (16), which could not rearrange to 14 or 15.

A series of model compounds for structures 1, 3, 4, 5, and 6 are being synthesized and will be reacted with maleic anhydride to test these hypotheses.

Conclusions

Maleation of PPE occurs by several different mechanisms, mostly having to do with chain ends. Two of the structures do not seem to be related to the dialkylamino substituents on the PPE end group (D and E). Evidence for the *o*-quinomethide adduct (8) is seen in samples with high levels of amine. Structures 8, 14, and 15 are highly speculative and will be further investigated via model compounds.

Acknowledgment. We thank B. VanBuskirk for providing the sample of vacuum-stripped PPE and R. Brambilla for acquiring the NMR spectra. Helpful suggestions from Dr. W. B. Hammond and Prof. E. L. Eliel are gratefully acknowledged.

References and Notes

(1) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustace, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 6335. Aycock, D.; Abolius, V.; White, D. M. *Encyclopedia of Polymer Science and Technology*; John Wiley and Sons: New York, 1989; Poly(phenylene ether).
(2) Hay, A. S. *Polym. Sci. Eng.* **1976**, *16*, 1.
(3) Boldebuck, E. M. U.S. Patent 3 063 872, 1962. MacKnight, W. J.; Karasz, F. E.; Fried, J. R. *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: New York, 1978; Vol. 1.
(4) Locke, C. E.; Paul, D. R. *J. Appl. Polym. Sci.* **1973**, *17*, 2597.
(5) Brown, S. Y.; Orlando, C. M. *Encyclopedia of Polymer Science and Engineering*; John Wiley and Sons: New York, 1989; pp 169–189.
(6) Trivedi, N. C.; Culbertson, B. M. *Maleic Anhydride*; Plenum: New York, 1982; pp 199–202.
(7) Kuwahara, H.; Tokuzawa, T. Jpn. Patent 54/59724, 1984. Ueno, K.; Maruyama, T. U.S. Patent 4 315 086, 1982. Jalbert, R. L.; Grant, T. S. U.S. Patent 4 654 405, 1987. Akkapeddi, M. K.; VanBuskirk, B.; Brown, A. C. Int. Patent Pub. PCT WO88/08433, 1988.
(8) Risse, W.; Heitz, W. *Makromol. Chem.* **1985**, *186*, 1835.
(9) Kohan, M. *Nylon Plastics*; John Wiley and Sons: New York, 1973; p 105.
(10) White, D. M. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1972**, *13*, 373. White, D. M.; Nye, S. A. *Macromolecules* **1990**, *23*, 1318.
(11) Campbell, J. R.; Hobbs, S. Y.; Shea, T. H.; Watkins, V. H. Presented at Polyblends, Boucherville, PQ, Canada, October 1989.
(12) Regel, W.; Schneider, C. *Makromol. Chem.* **1981**, *182*, 237.

Registry No. PPE (homopolymer), 25134-01-4; PPE (SRU), 24938-67-8; maleic anhydride, 108-31-6.