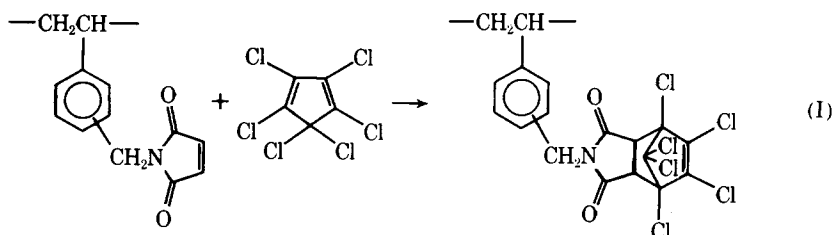


Reaction of Maleimidomethylated Polystyrene with Hexachlorocyclopentadiene*

INTRODUCTION

In a recent publication¹ we described the crosslinking of polystyrene that had been modified by incorporation of maleimidomethyl groups. Among the various crosslinking methods employed were Diels–Alder cycloadditions with a bisdiene and a pseudobisdiene. Because the Diels–Alder reaction of the pendent maleimide group occurred so readily, we investigated the analogous reaction (I) with hexachlorocyclopentadiene, with the expectation that the flammability of the polymer would be reduced. The results, which were only marginally successful, are described in this note.



EXPERIMENTAL

Quantitative reaction of hexachlorocyclopentadiene with maleimidomethylated polystyrene was accomplished by refluxing solutions of polymer in 1,2-dichloroethane (1 g per 10 ml solvent) in the presence of a threefold molar excess (based on equivalents of maleimide) of the diene for 3 hr. Modified polymers were precipitated in methanol, redissolved and reprecipitated, and dried at 60°C in a vacuum oven for 6 hr.

Flammability was determined by clamping thin films (4 × 0.75 × 0.001 in.) cast from 1,2-dichloroethane at a 45° angle and igniting the lower end for 2 sec with a microburner. Films were air dried for two days prior to testing.

Infrared spectra were determined on a Perkin–Elmer Model 457 grating spectrophotometer. Chlorine analyses were run at the Microanalytical Laboratory of the School of Molecular Sciences, University of Sussex, Falmer Brighton, U.K., and at Industrial Testing Laboratories, St. Louis, Missouri.

RESULTS AND DISCUSSION

Commercial polystyrene ($\bar{M}_n = 100,000$) modified with up to 18.4 mole % maleimidomethyl groups (based on phenyl) was used in this study. This results in a maximum chlorine content after quantitative reaction with hexachlorocyclopentadiene of 22.4%, a level reported² to make polymers flame retardant. Because maleimidomethylation can be achieved without difficulty¹ and because hexachlorocyclopentadiene is readily available, it was hoped that this Diels–Alder method of incorporating a relatively high chlorine content could be achieved without undue modification of the polystyrene backbone.

Quantitative reaction was carried out by refluxing polymer solutions in 1,2-dichloroethane in the presence of excess hexachlorocyclopentadiene. Infrared spectra of maleimidomethylated polystyrene before and after reaction with hexachlorocyclopentadiene are shown in Figure 1. Significant changes include the appearance of a carbonyl doublet peak at 1780 cm^{-1} , broadening of the major carbonyl

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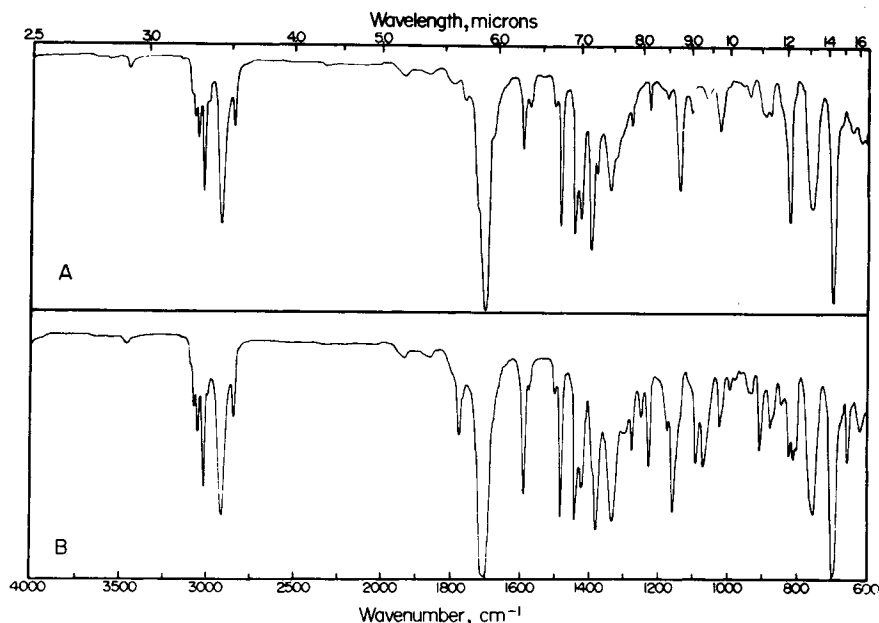


Fig. 1. Infrared spectra (films cast from 1,2-dichloroethane) of (A) maleimidomethylated polystyrene (18.4 mole percent substitution), and (B) sample A after reaction with hexachlorocyclopentadiene.

peak at 1700 cm^{-1} , and a decrease in the vinyl C-H out-of-plane bending absorption at 825 cm^{-1} . An increase in the intensity of absorption at 760 cm^{-1} and a new peak at 660 cm^{-1} are indicative of chlorine substitution.

A crude measure of flammability was determined by igniting film specimens for 2 sec. The results were disappointing. Although there was a progressive decrease in the time the flame traveled the 4-in. film length with increasing chlorine content (Table I), only sample 6 was self-extinguishing, and even this sample exhibited sustained but slow burning if longer ignition times were employed. A possible reason why flame resistance was less than expected may be that with thin films the availability of oxygen at the burning site is high because of the high surface area-to-weight ratio.

Differential thermal analysis (DTA) thermograms were measured for sample 6 ($20^\circ/\text{min}$ upheat rate in sealed capsules) as well as for polystyrene and maleimidomethylated polystyrene. The latter two exhibited endothermic transitions beginning at approximately 360°C , whereas sample 6 underwent a strongly exothermic decomposition (reverse Diels-Alder reaction) at 335°C . Because polystyrene is normally molded at about 200°C , these results suggest that the retrograde Diels-Alder reaction should not be a problem in a normal molding operation.

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TABLE I
Flammability of Chlorinated Polystyrene Films

Sample	% Chlorine	Burn time, sec ^b
1 ^a	0	2.1
3	8.0	4.3
4	15.8	4.6
5	20.0	5.1
6	22.4	self-extinguishing

^a Maleimidomethylated (18.4 mole-%) polystyrene.

^b Average of three samples. Test conditions described in experimental section.

References

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