

Quinone–Amine Polymers. VI. Syntheses and Solubilities of Several Cooligomers (PAQs) Produced by Reacting Two Diamines with *p*-Benzoquinone

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SYNOPSIS

The solubilities of some polyamine–quinone oligomers (PAQs) derived from various diamines were found to be incredibly low. Ethylene-diamine–*p*-benzoquinone products were insoluble in all 34 solvents used in assessing solubilities of polymers. Syntheses of copolymers/cooligomers of an amine yielding insoluble product with another that produces highly soluble amine were attempted. The increase in the solubilities of these copolymers/cooligomers as well as their appearances suggest that it is possible to produce PAQs from two different diamines.

INTRODUCTION

To bind to an unprepared, wet metal surface is a very significant property for a polymer¹; however, after curing it has to perform according to certain standards, such as resistance to salt spray for a certain period, resistance to abrasion, having acceptable flow, dry time, flash point, etc. No polymer can achieve these requirements without appropriate additives, but first and foremost a polymer has to be soluble in acceptable solvents. Jeffamine D-400–*p*-benzoquinone oligomers, represented as PAQ in this paper, meet many of these requirements, especially after the addition of certain chemicals.² It was quite natural, though, to look for other polymer/oligomers that might possess better properties. Since the characteristics of the amine used controls the overall properties of these polymers, this means preparation of different amine–quinone polymers and studying their characteristics, solubility in desirable solvents being the primary concern. As seen in the previous paper, however, very few diamine–benzoquinone polymers have satisfactory solubilities in common solvents. The first question that comes to mind, under these circumstances, is whether co-

polymers formed by reacting two amines with benzoquinone, might have greater solubilities in the common solvents used due to the introduction of irregularities into the chains. It has to be pointed out here, however, solubility alone is not enough to determine whether a polymer will produce a satisfactory coating. For this reason we had adopted a few additional criteria, albeit quite qualitative, for screening the products obtained for this purpose. These involve coating 1 × 5 in. aluminum and steel coupons with the compound in question and testing its characteristics after heat cure, usually at 150°C, but sometimes at lower temperatures, for several hours. The tackiness, resistance to immersion into artificial sea water or into acetone, of the coating is then evaluated. The more quantitative aspects of these studies, performed according to ASTM standards, will be published at a later date. In this paper the results of the experiments directed at the synthesis of copolymers and some of their characteristics will be described.

MATERIALS AND METHODS

The sources of chemicals and solvents used were described in the previous paper.

UV spectra were obtained using a Hitachi-Perkin Elmer Model 200 recording spectrophotometer.

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Figure 1 UV spectrum of the cooligomer formed by the reaction of Jeffamine -2000 and trimethylhexamethylene diamine with *p*-benzoquinone. The 344 nm peak represents substituted quinones and the 291 nm one probably the presence of hydroquinone.

Viscosities were measured using a Ubbelohde viscometer. Solubilities were determined by weighing a known amount, in different solvents, which was allowed to stand, with stirring and filtering the insoluble material, washing, and weighing.

General Procedure for the Synthesis of Cooligomers Consisting of Two Diamines and *p*-Benzoquinone

Feed ratio in all cooligomers was diamines: benzoquinone = 2 : 3. Both amines were used in equimolar amounts. Amines as well as benzoquinone were dissolved in THF to give a 10% (w/v) final concentration. Amine solution was added into quinone solution in a three-necked round-bottom flask equipped with reflux condenser, dropping funnels and a stirrer, over a period of 15 min, without allowing the temperature to rise above 30°C. The mixture was refluxed for 4.5 h; then most of the THF was removed, under vacuum. The remaining viscous solution was poured into excess water to precipitate the product, which was washed extensively with water until the wash water remained colorless. The sample was then dried in a vacuum oven at 55–60°C overnight.

RESULTS AND DISCUSSION

It is clear that two amines with widely different chemical structures react with *p*-benzoquinone quite

Table I Synthesis and Solubilities of Products Formed by Reacting Two Diamines with *p*-Benzoquinone

Amines (1 : 1)	Yield ^b (%)	Solubility % (w/w) ^c			Form	Qualitative Evaluation of Heat-Cured Films
		MEK	Ethanol	<i>n</i> -Butanol : Xylene		
1-Jeffamine D-2000-TMHMD ^a	67	29	20	16	Viscous liquid	Slightly tacky film
2-Jeffamine D-2000-ethylenediamine	44 ^d	23	18	24	Paste	Slightly tacky despite 8 h cure
3-Jeffamine D-400-TMHMD	86	23	32	33	Tough solid	Film appears nonwetttable by water, PAT 3–4 ^e
4-Jeffamine D-400-1,12- diaminododecane	93	9.2	3.65	9.2	Tough solid	Presence of solid particles, film nontacky PAT 4

^a TMHMD = trimethylhexamethylenediamine.

^b Assuming both amines have similar reactivities.

^c *n*-Butanol : xylene = 1 : 4.

^d Some polymer was lost during washings.

^e Paint adhesion test.

readily to produce cooligomers. UV spectra of the products exhibit the same absorption peaks as the pure oligomers (Fig. 1). At this moment it is not known whether the product is a pure cooligomer or a mixture of two oligomers. However, the results of solubility studies show that there is a spectacular increase in the solubilities of coproducts stemming from ethylene diamine and 1-12-diaminododecane compared to that of the single components. It is highly doubtful whether just a mixture of any soluble polymer with these highly insoluble pure oligomers could increase their solubilities to such high levels (see the previous paper³). When ethylenediamine oligomer was stirred in a solution of Jeffamine D-400 for 5 days, a decrease in the solubility of the former was observed, supporting the view that the increased solubility observed of these products is evidence of true cooligomer formation. The physical appearance of cooligomers, too, support the view that new products are formed. For example, Jeffamine D-2000 produces a very tacky coating even after prolonged heat cure, including hardeners,² whereas Jeffamine D-400 yields nontacky, extremely smooth films.¹ The first product listed in Table I, too, is a

viscous liquid the second is a paste, while products 3 and 4 produced from Jeffamine D-400 are solid. Similarly, films produced by the first and second products are slightly tacky while those stemming from products 3 and 4 are nontacky and nonwett-able. It is, on the other hand, quite conceivable that together with cooligomers, some pure oligomers, too, could form and remain either as a solution or a suspension in the bulk of the cooligomer. This question is being investigated further.

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