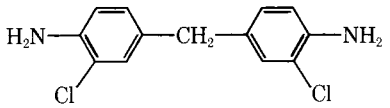
On the Use of Trimethylene Glycol Di-p-aminobenzoate as a Curing Agent for Polyurethane Elastomers

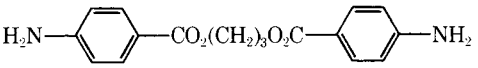
Recently, there has been considerable concern in the chemical industry about the carcinogenicity of many chemicals. One such chemical is 4,4′-methylenebis(2-chloroaniline), I, known to the elastomer industry by the acronym MOCA. This compound is a valued coreactant and curing agent for the isocyanate-terminated polymers such as "Adiprene" elastomers[1]:



I

Last year, the Occupational Safety and Health Administration, OSHA, placed MOCA on an emergency list of 14 chemicals which now require very special handling due specifically to allegations that the compounds cause cancer.[2] Because of this, there has been much concern with replacing MOCA, especially with a nontoxic material that will produce similar or superior polymers but with little change in processing conditions.

In our laboratory, we have synthesized an interesting diamine that we believe holds considerable promise as a MOCA substitute. The compound[3] is trimethylene glycol di-*p*-aminobenzoate, II:



II

In cooperation with Stephens Molded Products, Easthampton Massachusetts, our preliminary investigation has produced, in plant equipment, polyurethanes with excellent physical properties using compound II as a direct MOCA replacement. The prepolymers were of both the polyether type (Adiprene L-100, du Pont) and the polyester type (PCA-407, Polyurethane Corporation of America). Compound II has an equivalent weight of 157 and a melting point of 125–128°C. The compound is very stable to cleavage in the melt and is highly soluble in a variety of coating solvents. Compound II does not rearrange at elevated temperatures to the amide. It also shows the desirable property of having a melt that supercools. Cures are generally carried out at lower temperatures than customary with MOCA, and the pot life is excellent.

We considered the possibility that the unique properties of II might possibly be due to liquid crystal formation in the melt, especially when phenylene di-*p*-aminobenzoate was recently reported to show such behavior.[4] Professor Schroeder has kindly studied compound II at our request and has reported no evidence of liquid crystallinity.

Materials of the di-*p*-aminobenzoate type have been patented,[5] but in the context of *o*-chloro substitution, which we find to be neither necessary not desireable. The unsubstituted ortho-amino derivatives have been patented recently,[6] with the observation that the amino group in this position has a diminished reactivity similar to a para-amino derivative with a chlorine atom ortho to the amino group. We agree with this finding and also find that the meta-amino derivatives are too reactive. However, we are reporting here that the unsubstituted para-amino derivatives also show a decreased reactivity and we conclude the effect is electronic and not steric. We prefer the para derivatives since there are no possibilities of side reactions occurring on curing due to cyclization as is possible with the ortho derivatives since they are anthranilates. We also find that the preferred para derivatives with an even number of carbon atoms in the glycol portion have melting points which are too high. This series of compounds shows the well known "odd-even" relationship with melting point. The next most promising candidate synthesized in our laboratories is pentamethylene glycol di-*p*-aminobenzoate, although the compound is not a direct replacement for MOCA in the preparations we have tried. Compound II does not seem to have been described previously. The isomeric compound, from 1,2-propanediol, is a known com-

pound,[7] but gave poor elastomers in our hands and was not a good MOCA substitute.

Compounds of this type can be synthesized in good yields in two steps; namely, reaction of *p*-nitrobenzoyl chloride with the desired diol followed by reduction of the nitro group to the amine.

Our initial testing as to the acute toxicity of compound II show it to be nontoxic to rats. Although we have no long-term carcinogenicity testing data, it is worth noting that esters of *p*-aminobenzoic acid are in wide use as suntan oil additives and local anaesthetics.

References

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