

# Water-Soluble Photocurable Elastomer

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## Synopsis

A low molecular weight copolymer of vinylbenzyl chloride and butadiene was quaternized with N-dimethylaminoethylmethacrylamide. The resin was coated from water solution to give a photorelief plate which could be developed with water. A photocured protective coating on steel showed good toughness.

## RESULTS

A water-soluble photocurable elastomer was made by the quaternizing with dimethylaminoethyl (or propyl) methacrylamide of a low molecular weight copolymer of vinylbenzyl chloride and butadiene. The ratio of vinylbenzyl chloride to butadiene was varied depending on the objective. When the purpose was to make a photorelief plate which could be developed with water, the choice was the range of 40–50 wt-% vinylbenzyl chloride. When a water-resistant coating was desired, a lower content was used, for example, 20–30 wt-%. This still gave enough hydrophilic character so that the elastomer could be coated from an aqueous medium. A low molecular weight ( $M_w$ ) in the range of 10,000–30,000 was desirable for several reasons. It was necessary to give readily flowable concentrated solutions (for example, 30%) needed to cast the thick (20 ml) coatings used in relief plates. It was important also that unexposed areas be cleanly dissolved away during developing. It was found in practice that a molecular weight in this range was not easy to make by emulsion polymerization with the usual chain transfer agents. Dodecyl mercaptan has a sufficiently large chain transfer constant, but generally molecular weights in excess of 50,000 are obtained with it. Apparently, it is not transported to the locus of polymerization in sufficient concentration. In principle, one could use solution or suspension polymerization and thereby ensure the presence of sufficient chain transfer agent. In practice, however, butadiene polymerizes poorly in solution or suspension. The rate is very slow and the conversion necessarily incomplete.

The use of a high oil-to-water ratio, which resulted in inversion during emulsion polymerization, gave the desired low molecular weight polymer without achieving high conversion. Except for somewhat higher rate, the polymerizations in this medium resembled solution polymerization.

Benzyl mercaptan is reported<sup>1</sup> to have a higher chain transfer constant than dodecyl mercaptan. It was found that benzyl mercaptan could be used to obtain the desired low molecular weight in a true emulsion polymerization. The stench disappeared during the polymerization. The less objectionable 3,4-dichlorobenzyl mercaptan was used effectively but did not give as low a molecular weight as did benzyl mercaptan. Benzyl mercaptan produced some retardation of polymerization.

The high polymerizability of butadiene in emulsion polymerization is assumed to be due to restricted termination. It is of interest that precipitation polymerization with  $\gamma$ -ray initiation went to a high conversion. The polymer which phased out was subject to crosslinking, and the concentration of precipitant needed to get soluble polymer was critical.

Residual butadiene is readily removed, but residual vinylbenzyl chloride poses more of a problem. It can be steam distilled, but this procedure produces a considerable degree of hydrolysis.

The unsaturated amine that was used to quaternize the copolymer was made by the procedure of Barron by heating methacrylic acid with dimethylaminoethylamine or 3-dimethylaminopropylamine.<sup>2</sup> The monomer was distilled under conditions which caused rearrangement of any amine that had added to the double bond. Any diamine which formed was removed by distillation; otherwise it caused crosslinking during amination of the polymer.

Quaternization of the copolymer was usually carried out in dioxane with gradual addition of water. It was possible but more difficult to aminate in water alone. It was preferable to remove excess unsaturated monomer by the precipitation in acetone of the quaternized polymer. Alternatively, it could be neutralized and allowed to remain. The physical properties of the cured coating were better if it was removed. It was important to use a basic antioxidant and agitation during amination and to ensure that air was supplied to all parts of the mixture; otherwise premature cure might occur in any oxygen-depleted region. The addition of water during the amination minimized the period of phase separation when oxygen supply was limited. With these precautions it was possible to carry out the amination in 2–4 hr at 60°C without polymerization.

The quaternized copolymer dried to a tough elastomeric layer. It did not become brittle or curl within the range of humidities experienced (20–50%), nor did it become extremely tender during washout. It could be photocured with a very low light exposure. Usually a photoinitiator such as a benzoin ether was added, but it was not altogether essential. The light used was provided by a 5 kW Berkey Ascor 30 in.  $\times$  40 in. vacuum printer with reflector, and the light was filtered by a glass plate. Alternatively, a fluorescent light source, an order of magnitude weaker, was used with a 10-sec exposure. As a comparative measure of cure speed, it was found that the widely used NAPP<sup>5</sup> photopolymer plate is exposed 4–6 sec without the negative and then 70 sec through the negative. The purpose of preexposure is believed to be to consume air dissolved in the photosensitive material. No preexposure was needed with the present plate. The cure extended to the base plate, and the retention of highlight or leader dots was good (see Fig. 1).

When the molecular weight of the copolymer was too high (for example,  $\bar{M}_w = 50,000$ ) the photorelief layer tended to cure in the unexposed areas and cause plugging of the shadow dots. When the molecular weight was too low (for example,  $\bar{M}_w = 5000$ ), the cured relief lacked toughness. With an intermediate molecular weight (for example,  $\bar{M}_w = 25,000$ ), the shadow dots washed clean and the photorelief was tough.

The solubility in water of the aminated copolymer depended on the degree of quaternization. This was measured by a chloride titration of the reprecipitated derivative. When the equivalent weight per chloride was 400–600, the solubility and rate of dissolution in water were very good. When the equivalent weight was over 1000, it was necessary to use aqueous acetone or aqueous alcohol to dissolve the derivative.



Fig. 1. Tone scale and image made with the photo printing plate.

In Table I are given copolymer molecular weights as estimated by GPC in tetrahydrofuran. The figures quoted are based on calibration with narrow-distribution polystyrene samples. To the extent that the copolymers of this work contained butadiene, their molecular weight was therefore overstated and to the extent that they contained vinylbenzyl chloride, understated. The molecular weight values of Table I refer to latex polymers made with variations from the typical recipe as given in the experimental section and used for samples 2, 25, and 45; the variations are shown in Table II. The polymerizations were not taken to complete conversion; for example, the conversion in the run designated 6 was 85%; run 45, 80%; run 48-2, 25%.

An alternative method of making low molecular weight copolymer is by precipitation polymerization. The copolymerization of equal weights of vinylbenzyl chloride and isoprene in 20 vol-% methanol solution went to high conversion with 25 mrad  $\gamma$ -ray exposure (0.25 mrad/hr) and gave precipitation of a gum ( $\bar{M}_w =$

TABLE I  
 Copolymer Molecular Weights

Sample no.	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$
38-2	225	114
3	151	27
4	77	25
45	52	20
2	54	24
6-1	57	21
33-2	22	12
33-2	22	12
48-2	8.9	0.51
22-1	27	16
11-1	24	14

 TABLE II  
 Recipe Variations for Copolymers Listed in Table I

Sample no.	Variation
38-2 <sup>a</sup>	0.8 g CBrCl <sub>3</sub> added, CCl <sub>4</sub> omitted
38-3 <sup>a</sup>	dodecyl mercaptan omitted, 0.8 g CBrCl <sub>3</sub> added
38-4 <sup>a</sup>	all three chain transfer agents
6	ratio vinylbenzyl chloride to butadiene 0.50 by wt
11-1	oil-to-water ratio 7; 66°C
22-1	oil-to-water ratio 7; 66°C
33-2	oil-to-water ratio 7; 66°C; 40 cc toluene added
48-2	0.8 g benzyl instead of dodecyl mercaptan
	0.8 g 2,4-dichlorobenzyl mercaptan

<sup>a</sup> These were ternary copolymerizations made with 20 g vinylbenzyl chloride, 20 g styrene, and 40 g butadiene.

5700,  $\bar{M}_n = 2500$ ). Along the side walls of the ampule there was a coating of crosslinked polymer. Precipitation polymerization can be carried out also with homogeneous catalysts and the skin effect avoided.

One can substitute isobutylene for butadiene and use cationic copolymerization, but in this case isopropenylbenzyl chloride is a preferred comonomer as taught previously.<sup>3</sup> The better  $r_1, r_2$  match gives better uniformity.

One can substitute 2-chloromethylbutadiene for vinylbenzyl chloride and use it either as a copolymer or homopolymer.<sup>4</sup> The homopolymer coating had tack; therefore, the use of a comonomer such as styrene was preferred. A slight tackiness of the cured relief printing plate was controlled by using a second light exposure after development or by dusting the plate surface with a release agent such as magnesium oxide. It was not a problem unless the diene content was high.

It was possible to dilute the resin with a cheaper compatible water-soluble polymer and still retain fair imaging quality. Some of the diluents that were tested were polymers of oxazolines, poly(methyl vinyl ether), poly(vinylpyrrolidone), low molecular weight unhydrolyzed polyacrylamide, poly(dimethylacrylamide), and poly(vinyl alcohol), the polyamide of adipic acid and diethylenetriamine, and also gelatin below the isoelectric point. There were, however, disadvantages of the diluted resin. Gelatin, for example, contributed brittleness at low humidity and reduced adhesion to a plastic substrate such as Mylar. The

polyoxazolines, when used in equal weight, increased the necessary light exposure fivefold. Poly(2-methyloxazoline) was slightly more compatible than poly(2-ethyloxazoline).

Actually, some incompatibility in such mixtures could be tolerated. It produces turbidity, but the presence of some turbidity has the advantage of diffusing collimated light and producing a shoulder which helps to anchor dots that are isolated (see Fig. 2). Excessive incompatibility reduces toughness and is undesirable.

### DISCUSSION

It was possible to dry the layers in yellow light provided air was not excluded. It was surprising that there was no need to exclude air during the photocuring of the layers.

This photorelief plate differs also from others in common use in that it is not necessary to preexpose the plate without the negative in order to consume oxygen or other inhibitors. Without the preexposure, the commonly used photorelief plates do not develop the necessary shoulder to strengthen isolated or highlight dots. If an inhibitor other than oxygen is added to a plate which does not require preexposure, it may also prevent the development of shoulders.



Fig. 2. Enlargement of dots showing shoulder.

The present material is not totally unaffected by oxygen. For example, if it is exposed through a negative under nitrogen and then developed, there tends to be plugging of bowls (such as the hole in letter O). In view of the inhibitory effect of oxygen upon methacrylamides in general, it seems likely that the relatively small effect herein observed is due either to the consumption of oxygen by auto-oxidation of the side chain or to a low solubility of oxygen in the material because of its ionic character. There is, however, an interesting photosolubilizing effect caused by low exposures to fluorescent light. This is believed to be due to scission of polymeric peroxide. The formation of peroxide can be prevented by the use of hydroquinone.

In addition to the above cause of shoulder formation, in which oxygen is depleted in the deeper zone, it is possible to create shoulders deliberately introducing turbidity into the material to scatter light.

The usefulness of the butadiene-rich derivative as a radiation-cured metal primer was somewhat reduced by the presence of the chloride ion and the effect of it on protection of iron against corrosion and water in salt spray. It was possible to exchange the chloride for an anion that causes less corrosive action on steel. The polymer was coacervated with tripolyphosphate or hexametaphosphate and the salt rinsed out. The polymer could be redissolved in hot water because of hydrolysis of the polyphosphate to phosphate.

## Experimental

### Emulsion Polymerization Procedure

Laboratory polymerizations were carried out in citrate bottles with agitation for 16 hr provided by a rotor immersed in hot water at 60°C and suitably shielded. The typical recipe was as follows: azobisisobutyroamide hydrochloride,<sup>7</sup> 1.6 g; Arquad 12 50% aqueous solution, 0.8 g; dodecyl mercaptan, 0.8 g; carbon tetrachloride, 8.0 g; vinylbenzyl chloride, 40.0 g; butadiene, 40.0 g; water (deionized), 120.0 g. The latex was coagulated with methanol and redissolved in dioxane without drying.

### GPC Measurements

A Waters 200 instrument was used with tetrahydrofuran as the solvent, Styragel packing, and the UV detector at 265 m $\mu$ . The spreading correction of Tung<sup>9</sup> was applied. No correction was made for the higher hydrodynamic radius of polybutadiene versus that of polystyrene.<sup>10</sup>

By titration of latex made without the addition of chloride ion it was found that 15% of the vinylbenzyl chloride hydrolyzed during the polymerizations.

### Amination

A solution (30%) of the copolymer in dioxane was treated with an excess of N-dimethylaminoethylmethacrylamide (an equal weight on a dry basis). After a day at room temperature a gel had formed. It dissolved on the addition of water and was precipitated with acetone. A small amount of salt was added to aid filtration. The polymer was soluble in aqueous ethanol and was coated from this solution.

The equivalent weight per chloride was determined by titration with silver nitrate. For the ternary copolymers designated in Table I as 38-2, 3, and 4, the equivalent weights were 2126, 2220, and 1260, respectively. Photorelief layers made from these resins imaged well but did not wash well.

The binary copolymer designated 45 was aminated in 10% dioxane solution at 50°C and with a 1½ weight ratio of dimethylaminoethylmethacrylamide and 0.3% diphenylamine as antioxidant. Gradual additions of water were made during the amination in order to keep the resin from precipitating. After 2 hr the derivative was found to have a chloride equivalent weight of 1060. The layer made from this resin could be developed with water but only if it was used before fully dried. The amination was repeated for 15 hr at 40°C. The equivalent weight was 1007 (corresponding to 36% quaternization), and washing of the imaged coating was still not satisfactory.

The copolymer designated 6 was aminated to an equivalent weight of 733, whereas that calculated for complete amination was 615; nevertheless, the cured layer required on aqueous alcohol development. This copolymer was made from a butadiene-rich feed (Table II).

The low molecular weight copolymer designated 33-2 was quaternized at 40°C in 4 hr to an equivalent weight of 407. A 17-mil layer containing 2% Vicure 10(6) was cast and cured with a 5-sec exposure to a three-tube fluorescent light [3-30 w tubes F36T12-BL-HO(8)] at a distance of 1½ in. from the sample. The layer was readily developed with water at room temperature. There was excellent penetration of the relief between type, in type bowls, and in shadow dots. The leader dots were retained; some high-light dots were lost.

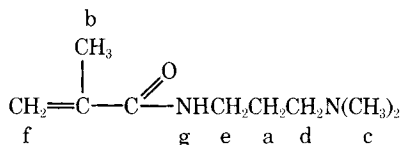
A low molecular weight copolymer (designated 11-1) (21.3 g) was stirred overnight at 40°C in dioxane solution (100 g) with dimethylaminoethylmethacrylamide (16 g) and diphenylamine (0.25 g). Water (25 g) was added after the first 2 hr and clarified the turbidity that had developed. The derivative was precipitated with acetone and, without drying, redissolved in water to give a slightly viscous 30% solution. The chloride equivalent weight was 565.

ANAL. Calcd: N, 7.72. Found: N, 5.56 (sample 25).

The copolymer 25 was quaternized as a latex with dimethylaminoethylmethacrylamide. The pH was adjusted from 8 to 5 with acetic acid. The chloride equivalent weight was 521. The solution was used for radiation-cured coating evaluation.

### N-(3-Dimethylaminopropyl)methacrylamide

Methacrylic acid (430 g) containing N,N-diphenylphenylenediamine (4 g) was treated gradually with 3-dimethylaminopropylamine. The mixture was heated at 300 mm pressure and distilled water (40 g). The monomer was distilled at 105-10°C at 2 mm pressure with no fractionating column. It contained a trace of the *o*-hydroxyisobutyramide as shown by NMR (CH<sub>2</sub>OH at 3.3 ppm, CH<sub>3</sub> at 1.15 ppm).



ppm in CDCl<sub>3</sub>, 60 m cycle NMR: a, 1.5; d, 2.4; g, 7.9.  
b, 1.9; e, 3.0; c, 2.2; f, 5.5

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