

References

1. Solomon, O. F., and I. Z. Ciută, *J. Appl. Polymer Sci.*, **6**, 683 (1962).
2. Huggins, M. L., *J. Am. Chem. Soc.*, **64**, 2716 (1942).

E. H. CATSIFF

Thiokol Chemical Corporation
Trenton, New Jersey

Received April 4, 1963

Investigation of the Effect of Chloronitroso Compounds on Polymers Irradiated with UV Light

The investigations of Hammick and Lister,¹ of Mitchell, Schwarzwald, and Simpson² and others have shown that in the presence of UV light chloronitroso compounds are decomposed easily with the formation of H and Cl radicals. The presence of strongly

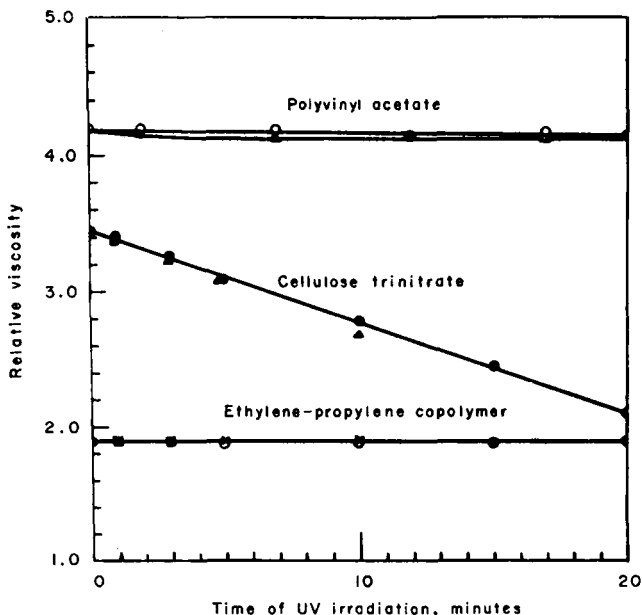


Fig. 1. *Polyvinyl acetate* (the solvent was ethanol): (Δ) Polyvinyl acetate with (I), and (\circ) polyvinyl acetate without (I). Weight concentration of (I) in solution was 0.117%, and the weight concentration of polyvinyl acetate in solution was 2.36%. Molar ratio (I): vinyl acetate mer = 0.029. *Cellulose trinitrate* (the solvent was acetic acid): (\blacktriangle) Cellulose trinitrate with (I), and (\bullet) cellulose trinitrate without (I). Weight concentration of (I) in solution was 0.09% and the weight concentration of cellulose trinitrate in solution was 0.906%. Molar ratio (I): cellulose trinitrate mer = 0.232. *Ethylene-propylene copolymer* (the solvent was benzene): (\times) Ethylene-propylene copolymer with (I), and (\circ) ethylene-propylene copolymer without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of ethylene-propylene copolymer in solution was 1.88%. Unknown composition of the copolymer.

electronegative chlorine atom and of the nitroso group at the same carbon atom suggested the possibility, that such compounds may form links with double bonds, and that such links may be disrupted by incident light quanta. This disruption may be accompanied by the disruption of the double bond. In this way the respective chloronitroso compound may act as a sensitizing agent for the photochemical reaction of depolymerization.

Systematic investigations of the above process have been started. At first the effect of chloronitrosocyclohexane (I) on a number of polymers dissolved in suitable solvents has been examined. The measurements of relative viscosity of the solutions show, that the polymers can be divided into three groups:

(1). Polymers which are not altered by the addition of (I) and irradiation with UV light (Fig. 1). Polyvinyl acetate, cellulose trinitrate, and ethylene-propylene copolymer among others belong to this group.

(2). Polymers which are slightly altered by the addition of (I) and UV light irradiation (Fig. 2). This group includes polymethylmethacrylate, polybutylmethacrylate, polyisobutene, and polystyrene.

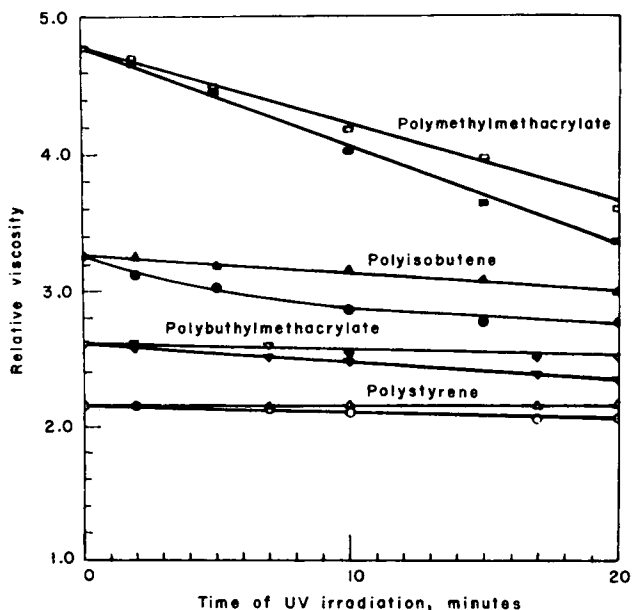
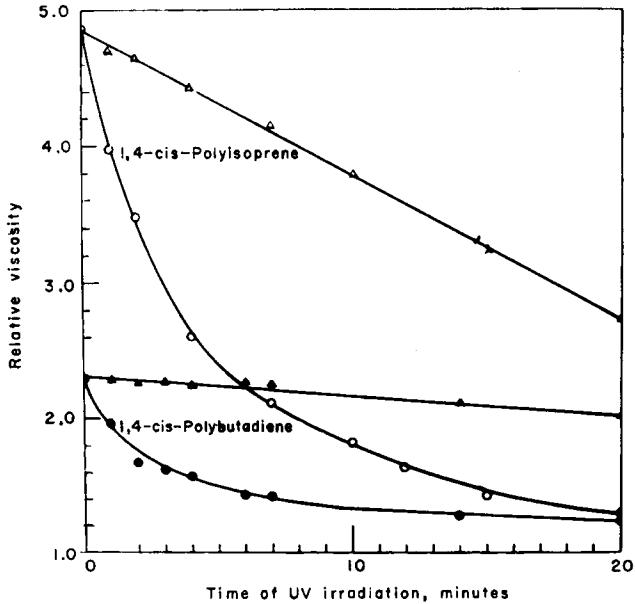


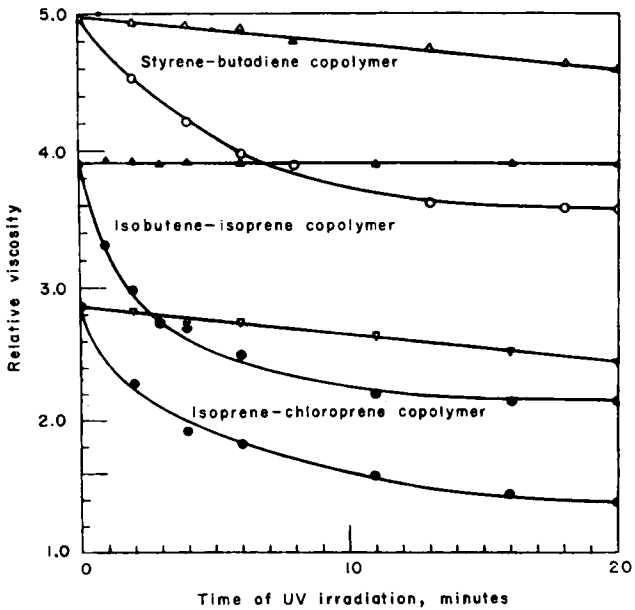
Fig. 2. *Polymethylmethacrylate* (the solvent was acetone): (■) Polymethylmethacrylate with (I), and (□) polymethylmethacrylate without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of polymethylmethacrylate in solution was 0.70%. Molar ratio (I): methylmethacrylate mer = 0.116. *Polyisobutene* (the solvent was gasoline): (●) Polyisobutene with (I), and (▲) polyisobutene without (I). Weight concentration of (I) in solution was 0.115%, and the weight concentration of polyisobutene in solution was 2.36%. Molar ratio (I): isobutene mer = 0.0185. *Polybutylmethacrylate* (the solvent was toluene): (▼) Polybutylmethacrylate with (I), and (▽) polybutylmethacrylate without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of polybutylmethacrylate in solution was 0.29%. Molar ratio (I): butylmethacrylate mer = 0.399. *Polystyrene* (the solvent was toluene): (Δ) Polystyrene with (I), and (○) polystyrene without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of polystyrene in solution was 1.11%. Molar ratio (I): styrene mer = 0.076.

(3). Polymers which are considerably affected by the presence of (I) and UV radiation (Figs. 3A and 3B). Natural rubber, 1,4-*cis*-polybutadiene, 1,4-*cis*-polyisoprene and copolymers styrene-butadiene, isobutene-isoprene, isoprene-chloroprene.

The above findings indicate that chloronitroso compounds affect in the first place the polymers containing double bonds. A very high decrease of relative viscosities after



(A)



(B)

the addition of even very low amounts of (I) (molar ratio of (I) to the monomer = 0.0115:1.0) suggests a sensitizing process. The decrease of relative viscosity after the addition of (I) depends upon the quantity of incidents light quanta. The decrease of viscosity discontinues when the light is switched off. In absence of UV light addition of (I) does not produce viscosity decrease for about 20 hr.

The investigations of the reaction mechanism are continued with IR and UV spectroscopic methods. The effect of other chloronitroso compounds, such as chloronitrosopropane and chloronitrosomethane, has been examined also.

References

1. Hammick, D. Ll., and M. W. Lister, *J. Chem. Soc.*, **1937**, 489.
2. Mitchell S., K. Schwarzwald, and G. K. Simpson, *J. Chem. Soc.*, **1941**, 602.

J. F. RABEK
T. I. RABEK

Department of Plastics Technology
Technical University of Wrocław, Poland

Received February 11, 1963

Fig. 3. (A) *1,4-cis-Polyisoprene* (the solvent was benzene): (O) *1,4-cis-Polyisoprene* with (I), and (Δ) *1,4-cis-polyisoprene* without (I). Weight concentration of (I) in solution was 0.109%, and the weight concentration of *1,4-cis-polyisoprene* in solution was 0.340%. Molar ratio (I): isoprene mer = 0.1480. *1,4-cis-Polybutadiene* (the solvent was benzene): (\bullet) *1,4-cis-Polybutadiene* with (I), and (\blacktriangle) *1,4-cis-polybutadiene* without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of *1,4-cis-polybutadiene* in solution was 0.479%. Molar ratio (I): butadiene mer = 0.0918. (B) *Styrene-butadiene copolymer* (the solvent was benzene): (O) *Styrene-butadiene copolymer* with (I), and (Δ) *styrene-butadiene copolymer* without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of *styrene-butadiene copolymer* in solution was 1.29%. Unknown composition of the copolymer. *Isobutene-isoprene copolymer* (the solvent was benzene): (\bullet) *Isobutene-isoprene copolymer* with (I), and (\blacktriangle) *isobutene-isoprene copolymer* without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of *isobutene-isoprene copolymer* in solution was 2.56%. Unknown composition of the copolymer. *Isoprene-chloroprene copolymer* (the solvent was benzene): (∇) *Isoprene-chloroprene copolymer* with (I), and (∇) *isoprene-chloroprene copolymer* without (I). Weight concentration of (I) in solution was 0.12%, and the weight concentration of *isoprene-chloroprene copolymer* in solution was 1.15%. Unknown composition of the copolymer.