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CROSS-LINKING OF METHACRYLATE POLYMERS BY ULTRAVIOLET RADIATION

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The durability of coatings is generally judged on the basis of discoloration or mechanical failure. In seeking thermoplastic polymers which, in addition to being highly resistant to discoloration and mechanical failure, also retain their solubility in petroleum hydrocarbons over long periods of time, our laboratory found that certain members of the methacrylate family cross-link under the influence of light and heat in advance of visible failure of the coatings.

The ability of "butyl" polymethacrylate to form a tri-dimensional polymer under the influence of heat, has been reported by Drinberg and Yakovlev.⁽¹⁾ In 1955, Reynolds,⁽²⁾ investigating the depolymerization of poly(isoamylmethacrylate)⁽³⁾ at 160 to 200°C. in this laboratory, observed that within 10 to 20 hours the film had become insoluble in hot benzene and toluene. At that time, a report of a paper by Shultz and Bovey,⁽⁴⁾ stating that poly(t-butyl acrylate) did not cross-link under the conditions of their experiments and one by Wall⁽⁵⁾ stating that poly(methylmethacrylate) did not cross-link during degradation, prompted the writer to question the behavior of the other members of the methacrylate family and to investigate the effects of ultraviolet radiation.

RESULTS OF EXPOSURE IN FADEOMETER

At first, simple tests were made of the ability to remove the films with solvents. This was done by rubbing with cotton swabs, twisted on the end of a probe and dipped in solvent. "Resistance to solution" was taken when the time required to dissolve, or otherwise wear away, the 1 to 3 mil-thick film through to its support required 75 to 105 seconds. Results of exposure in a National Accelerated Fading Unit Type XV, to radiation from a National Sunshine Carbon arc with Corex D filter, are summarized in Table I. Samples attained temperatures of about 60°C. during exposure.

The shortest wavelengths of ultraviolet radiation are most responsible for these reactions. In tests upon the p-methyl-cyclohexyl/isoamyl copolymer, isobutyl, and isoamyl polymers, it was demonstrated that a filter of ordinary window glass increased the lifetime of these polymers in the fadeometer by a factor of 1.9.

Films were cast on aluminum foil from solution in toluene, allowed to stand for several days and baked at 70°C. in a Fisher "Iso-temp" oven for two or three days before exposure. The isobutyl and n-butyl polymers were du Pont "Lucite" 44 and 45. Other polymers were prepared by Reynolds⁽⁶⁾ by polymerization in solution using benzoyl peroxide initiator. The method of measurement is related to the technique of removing coatings from objects of art and is sufficient to

demonstrate that certain of the polymers, originally removable in cycloparaffin hydrocarbons, are removed more slowly and with increasing difficulty during the course of exposure to ultraviolet light.

Apparently, methacrylate polymers having hydrogen atoms located on tri-substituted carbon atoms in the alkyl radical of the alcoholic group are sensitive to cross-linking under the action of ultraviolet radiation. The preparation and testing of methacrylate polymers which do not have this structure has been undertaken.

ESTIMATION OF DURABILITY INDOORS

What do these results mean in terms of exposure to ordinary levels of daylight illumination indoors? The Harrison Report, published by the Metropolitan Museum of Art⁽⁷⁾ mentions eight standards of light-fastness, each representing a standard of durability double that of the one below. The report also stated that classification VIII was equivalent to between 930 to 1920 hours of sunlight and that 24 hours in the carbon-arc illumination is supposed to be equivalent to 60 hours of full sunlight. From these data, the following table may be established.

Table II

Exposure in Fadeometer Equivalent to Standards of Light-Fastness

Values Derived from L. S. Harrison⁽⁷⁾

Fastness	Standard	Hours in Fadeometer to Cause Noticeable Fading	Average Hours
Slight	I	3 - 6	4.5
	II	6 - 12	9
Limited	III	12 - 24	18
	IV	23 - 49	36
Satisfactory	V	46 - 99	72
Good	VI	93 - 197	144
Very Good	VII	186 - 384	285
Excellent	VIII	372 - 768	570

Durability of 250 hours, before resistance to solution in toluene occurs, would place a material in Classification VII. Equating 6 years in a "gallery without sun-louvers" to 72 + 27 hours of arc illumination for a class V dye,⁽⁷⁾ one may estimate 15 to 33 years before resistance to toluene would be developed by the isobutyl or isoamyl polymers in a gallery without sun louvers. (Attention is drawn to the lack of precision in such an estimate in that these figures would be 45 to 99 years, if one based the estimate on values for a "day-lighted gallery with sun-louvers properly operated", and a minimum of 200 years, if based on values for artificially-lighted galleries at 60 fc. level of illumination).

In outdoor exposure under window glass on the roof of Mellon Institute, films of poly(isobutylmethacrylate) of 50 centipoise viscosity grade and poly(isoamylmethacrylate) of 23 centipoise viscosity grade, cast on glass from petroleum hydrocarbons of boiling range 160 to 190°C., did not discolor or crack in one year, and were removable in toluene within two minutes of rubbing, but with considerable resistance. Comparing the exposure index for wall exhibits in day-lighted galleries without sun-louvers in Harrison's Table VI to an average (annual) exposure index for outdoor exposure in New York of 51.7 and allowing for the factor of damage per foot candle to be reduced to about 1/2 by a filter of window glass, one may estimate that one year on the roof is equivalent to about 24 years in a day-lighted gallery without sun-louvers.

Crude as these estimates are, figures of about 24 years suggest that, if isobutyl or isoamyl polymers were to be used in the care of museum objects, the problem deserves consideration. Methacrylate polymers have not been of interest to museums for more than about 18 years. Of these, the n-butyl polymer has been of more universal interest than the isobutyl. In a sense, an investigation now is in anticipation of a problem which might someday, but apparently has not yet, become important in removing protective coatings based on methacrylate polymers.

DETECTION OF CHANGE BY PAPER CHROMATOGRAPHY

How can one detect if a change has begun to take place in the polymers? Paper chromatography might indicate if the polymer had become of higher average-molecular-weight owing to cross-linking. Tests of polymers of different viscosity-grade suggested this technique would be useful. (8) Such a technique has been used to distinguish polyethylene oxides. (9)

Strips of 1 1/2"-wide Whatman No. 1 filter paper were used in a descending development. The solvent was a mixture of equal volumes of xylene and non-aromatic, naphthenic, petroleum of boiling range 170 to 190°C., density at 70°F, 0.81. Samples were removed from the test panels with a cotton swab and the swab applied to the marked origin. In five hours development the solvent front migrated to the extent of about 30 to 40 centimeters. The polymers generally developed in a streak, frequently extending to and including the original spot. Since the paper is "varnished" with the resin, spraying with an aqueous solution will reveal areas where the paper is not wet. A dye may be added to the water for permanent record.

Figure 1 shows a curve of Rf values relative to unexposed polymer, based upon the position of the most advanced tip of the polymer. Empirically, the data relates relative Rf to time of exposure. This technique differs from that of Thomson (10) in that he uses a good solvent for the polymer and seeks to sweep all but the insoluble (cross-linked) portion away. His use of stain in the developing liquid no doubt provides excellent reproducibility in revealing the developed pattern. The two techniques could be combined on one paper. After development of the "streak" in poor solvent, the origin could be examined by Thomson's technique.

Many inhibitors were tested. Few were satisfactorily soluble in hydrocarbons. Ultraviolet-absorbing compounds 2,4-dihydroxybenzophenone and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone were found to increase times in Table I by about 150 hours, in the case of the isoamyl, isobutyl, and n-butyl polymers in the presence of 0.5% inhibitor based on the weight of polymer. In Figure 1, the effectiveness of these two compounds and the lack of effect by 2-hydroxy-4-methoxybenzophenone in protecting poly(isoamylmethacrylate) is indicated by the results of chromatographic analysis.⁽¹¹⁾ The mechanism of inhibition by such compounds is discussed by Burgess.

The chromatographic technique should indicate if a significant change in a polymer is in progress. Values taken to demonstrate the technique and to determine if change had occurred in various samples exposed indoors in well-lighted rooms are given in Table III. The ten-year samples were taken from test panels at the Fogg Museum of Art, Harvard University, through the kind cooperation of Miss Elizabeth Jones of the department of conservation.

The lowest relative Rf values found for the isobutyl or isoamyl polymers exposed under normal conditions indoors were about 0.91 for five-year-old panels. If one assumes that the decrease in relative Rf will be linear, and that at a value of 0.5 the resistance to cyclohexane would become apparent when using solvents on a swab, the results imply that this state will arise in about 28 years of exposure similar to that which has already taken place. According to data in Table I, resistance to toluene by these polymers develops in about twice this time. This compares favorably with estimates based on exposures in the fadeometer.

Table III

Methacrylate Polymer	Aged in Years	Relative Rf
0.75 to 3.0 mg. of sample		1.00
8 cp. Isoamyl vs 23 cp. visc. grade		1.06
18 cp. Isobutyl vs 55 cp. visc. grade		1.08
n-Butyl	10	0.84 ± 0.05
Isobutyl/n-Butyl copolymer	10	0.79 ± 0.01
Isoamyl	4	0.95 ± 0.03
Isobutyl	5	0.93 ± 0.02
Isoamyl in condition of "resistance to removal in cyclohexane"		0.50 ± 0.10

SUMMARY

It has been shown that linear polymers of the methacrylate class, in which the alkyl radical in the alcoholic group of the methacrylic ester contains hydrogen atoms located on tri-substituted

carbon atoms, are sensitive to cross-linking under the influence of ultraviolet radiation. A filter of ordinary window glass reduces the rate of cross-linking of certain methacrylate polymers by a factor of about 1/1.9. The compounds 2,4-dihydroxybenzophenone and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone reduce the tendency of the isoamyl, isobutyl and n-butyl polymers to lose solubility in hydrocarbons.

A paper chromatographic technique has been described which permits measurement of the action by ultraviolet light on linear polymers during the early stages, before apparent failure of the film.

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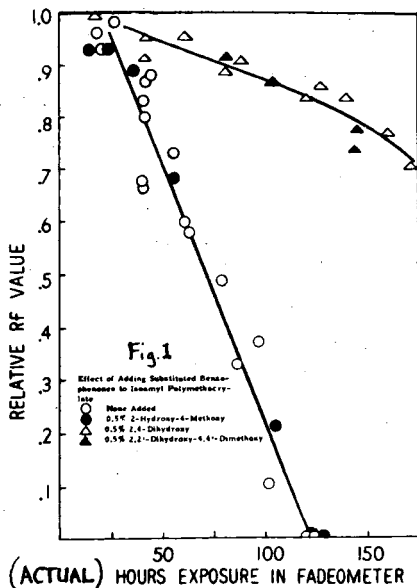


Table I

Hours of Exposure* of Methacrylate Thermoplastics Before Developing Resistance to Solution in Various Solvents

Alcohol Radical in Polymer	Viscosity Grade** of Polymer in Centipoises	Solvent		
		Cyclohexane	Toluene	Acetone
25/75 p-Methylcyclohexyl/Isoamyl Copolymer	18.5	50	130	
3-Methylbutyl	22	84	160	
Isobutyl, also 2-Ethylbutyl	50, 13	125	200	
Isoamyl (3)	23	133	250	~700
2-Methylbutyl	22	148	300	
n-Butyl	48	425	560	1100
n-Propyl	16		1050	
(Polyvinylacetate for comparison)	80		>1500	

* Actual hours multiplied by 1.9 to approximate effect of reflection from aluminum foil.

** Viscosity of solution in toluene of 20% solids by weight at 70°F.