Thoughts About "Crosslinking"

Thermoplastic and thermosetting polymers constitute the two broad classes of synthetic resins. The first is commonly visualized as strings of "monomeric" units linked together in long spaghetti-like chains; the second, a network in which the strings are linked together in a three-dimensional form. Depending on the extensiveness and rigidity of the network, the thermosetting class has provided numerous materials of outstanding toughness, hardness, and durability. In principle, such a structure cannot be dissolved, at best only swollen. Thermoplastics on the other hand are capable of being dissolved, the chains floated apart and dispersed in a solvent.

In the period 1930-50, several types of thermoplastic polymers of moderately high molecular weight were proposed as protective coatings for use in conservation, materials that held promise of remaining soluble and exhibiting little tendency to discolor over long periods of time: poly(vinylacetate) in the 1930s and, particularly after World War II, the polymers of isobutyl- and normal butyl- methacrylate.[1] In the 1950s there were several picture varnishes on the market based on the latter.

Early History

It was not long before the realization came to conservation scientists that some acrylic thermoplastics could develop "crosslinks" upon exposure to heat and light. Should this unwanted behavior occur over time, a coating could lose its ability to be re-dissolved or even to be appreciably swollen. The initial instance of crosslinking was encountered in films of the acrylic themoplastics following exposure in a carbon-arc fadeometer at high levels of ultraviolet and of temperature (about 62°C). Under milder conditions of exposure, such a chemical change was projected to take place much less readily, perhaps becoming detectable after about 18-28 years on a museum wall under diffuse daylight through window glass (1)(2).

The matter is of such interest to both the conservator and conservation scientist that it appears useful to review some of the history of the occurrence of crosslinking in these polymers, the photochemistry involved, and the various ways of measuring the extent to which it may take, or may have taken, place.

In October 1956, Garry Thomson published a note on a way to detect crosslinking(1).[2] Soon thereafter, the conference on picture varnishes held at Oberlin College, Ohio, in April, 1957, provided the opportunity to consider the subject in some depth (2). A number of the events that led up to the understanding of the crosslinking in the months just prior to the meeting have been described in the book derived from the conference, *On Picture Varnishes and their Solvents*, (2)(3).

[1] These possessed number-average molecular weight on the order of 20,000-50,000, forming solutions with about 20-50 times greater viscosity than the low-molecular-weight types AW2, MS2A, and dammar. Polymers of the latter class require many more crosslinks before the molecules can become large enough to form an insoluble matter.

[2] Thomson pointed out that poly(vinylacetate) has little tendency to crosslink; industry knew the same was true about the very successful product, poly(methylmethacrylate). Acryloid B72 has been found also to be highly resistant to loss of solubility (7)(12).

Shortly after the Oberlin conference, the types of acrylic polymers most prone to crosslink were shown to be those in which the alcohol moiety contained tertiary hydrogens; those with secondary hydrogens do so less readily (4)(5). By 1963, the basic studies on the subject were completed with the demonstration that the tendency to crosslink would be diminished as the middle and near ultraviolet and the shorter wavelengths of visible were reduced (6). Some years later, it was shown that crosslinking tended to follow the reciprocity principle (7).

Temperature

The high intensity of light normally used in accelerated photochemical procedures generally results in elevating the temperature of samples being tested. As a consequence, some polymers being tested may be subjected to temperatures that are above their second order or glass transition temperature, Tg, in one sense, their softening or melting point.[3] Temperature is known to affect crosslinking, yet full attention has not always been given to this aspect of testing.

For example, during a 1977 investigation of the effect of temperature during carbon-arc exposure, poly(isobutylmethacrylate) had been observed to undergo a different degree of crosslinking above and below its second order transition temperature, Tg (about 50°C) (Fig. 1) (9). At 60°C crosslinking occurred exclusively; at the lower temperature, 32°C, a ratio of about 7 breaks to 10 links had developed (β/α 0.7 in Fig.1). Unfortunately, other matters intervened at the time. and the matter was not pursued.

[3] Schilling has provided an extensive discussion of Tg (8).

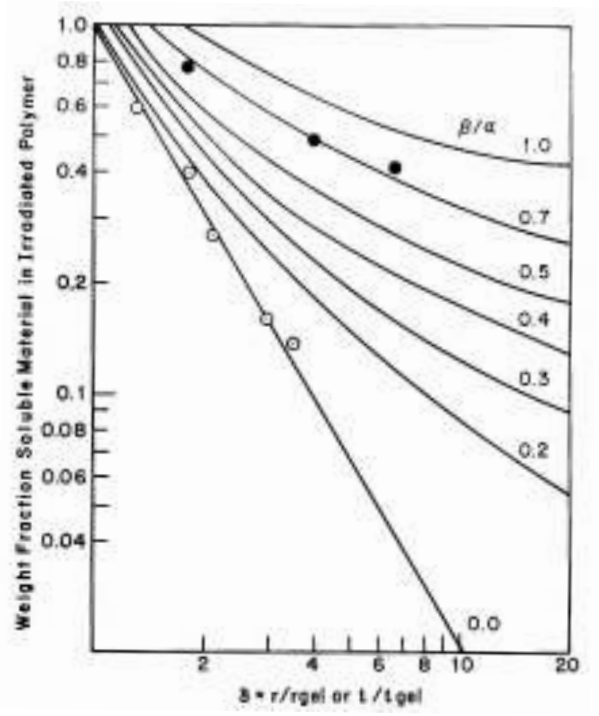


Figure 1. Loss of solubility data. Fadeometer exposure, poly(isobutylmethacrylate)(9).

● Data at 62°C ● Data at 32°C δ = gel time

Significance of Tg in Photochemical Studies

A recent photochemical study provided an opportunity to check this behavior in the case of another thermoplastic polymer, poly(vinylbutyral) (PVB) (10). Although PVB may not be of major interest as a surface coating, the Tg of the PVB studied, 63°C, readily allowed exposures to be conducted at temperatures both above and below that point. The resultant data, Fig.2, show crosslinking to have taken place exclusively when the PVB was above its Tg. At temperatures significantly below Tg, little if any insoluble matter developed.[4]

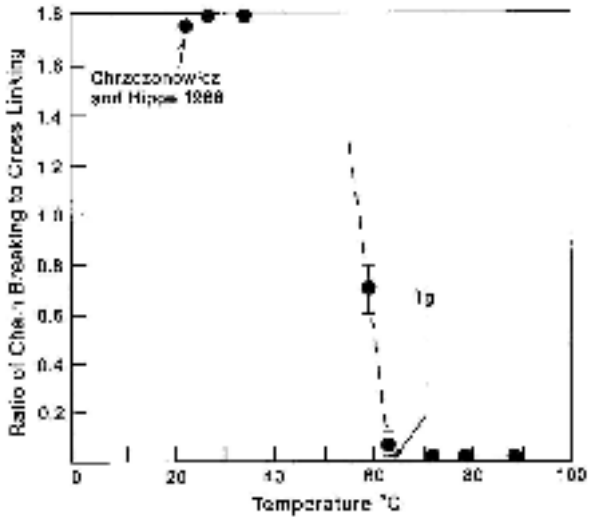


Figure 2. Ratio of chain breaking to crosslinking versus temperature. Poly(vinylbutyral) Butvar©B-79 exposed to near-ultraviolet BLB lamps (10).

This behavior is not a sharp "on and off" situation, however; intermediate degrees of chain breaking to crosslinking were noted at temperatures slightly on the lower side of Tg. Similar intermediate behavior is seen in Fig.1: at 62°C poly(isobutymethacrylate) exclusively crosslinked, but at 32°C a degree of both crosslinking and chain breaking occurred. As well, much the same intermediate behavior previously had been noted in the case of a copolymer of isoamyl- and methylcyclohexylmethacrylate (7).

This behavior has been known for some time; references can be cited to a number of well documented examples of the tendency for polymers to chain break below the Tg under various circumstances and to crosslink at temperatures above Tg (10). The explanation seems to be as follows: above Tg the polymer molecules, particularly any pendant groups extending much away from the main chain, are in considerable thermal motion. Thus, if a free radical (unshared electron) site is generated at some point in the initial polymer structure, the mobile situation would foster the chance to link up with a neighboring chain. On the other hand, at temperatures significantly below Tg, molecular motion is very much diminished, sometimes referred to as being "frozen." In this state, an unshared electron site created somewhere along the polymer chain is relatively immobile, literally having nowhere to go; instead of linking up, the chain tends to disintegrate at that point; it breaks. This is essentially the explanation given by Jacobs and Steele in the case of poly(ethylacrylate)(11).

Degrees of Crosslinking

In view of the many chemical processes that can take place during the aging of polymers, the possibility must always be considered that some degree of linking-up can occur between the initially un-linked chains. However, crosslinking need not proceed to the extent in which a large percentage of the initial polymer has become insoluble. Today the powerful tool of size exclusion chromatography (SEC) is able to detect whether even a very small fraction of the starting molecules has grown in size or has undergone chain scission. Chiantori and his associates have extensively applied SEC to many studies of the accelerated photochemical aging of many acrylics, the Acryloid © (Paraloid ©) polymers of Rohm and Haas being of particular interest (12)(13).

Considering the possibility of detecting even small amounts of crosslinking with such a technique, what then does someone really intend to convey when warning a conservator not to use the n-butyl-, isobutyl- methacrylate polymers, or the experimentally tested isoamyl variety "because they will crosslink"?

Perhaps one could define the situation more precisely by advising not to employ these specific polymers as a surface coating "because, under the conditions of normal usage they tend, not to undergo chain scission, but primarily to crosslink and therefore, in a specified number of years, might become x% insoluble in a specified solvent and to swell less than y%." It will remain for future research to determine whether a certain percentage of insoluble matter and limited degree of swelling is acceptable in conservation practice. Nonetheless, whatever cautionary statement is formulated, it is likely to remain a mouthful. As a consequence, one commonly has heard simply that a particular polymer "will crosslink." Certainly the subject needs amplification.

Swelling, Removability

Should a thermoplastic coating gradually become increasingly crosslinked, the material often still can be swollen and removed as a gel. Although one would wish ideally that formation of an insoluble fraction not take place, the ability to be swollen at least can be regarded as a safety factor in case crosslinking is found to have reached one of its early stages in the buildup of insoluble matter. A number of practical aspects regarding the removability of a coating under these conditions have been described elsewhere (Fig. 3)(3). In 1990, the National Gallery of Art reported the results of a major investigation on the removability of varnishes based on n-butyl and isoamyl methacrylate polymers after their having been under various museum conditions for a period of fourteen to forty years(14). The predictions made on the basis of accelerated aging tests were found to be essentially confirmed: all the varnishes

[4] Near-ultraviolet emitting BLB "black light" bulbs were used in order to speed up degradation. As another objective of the research, however, care was taken to show that very much the same degradative processes occurred whether UVB, UVA, or daylight fluorescent (DLF) lamps were used.

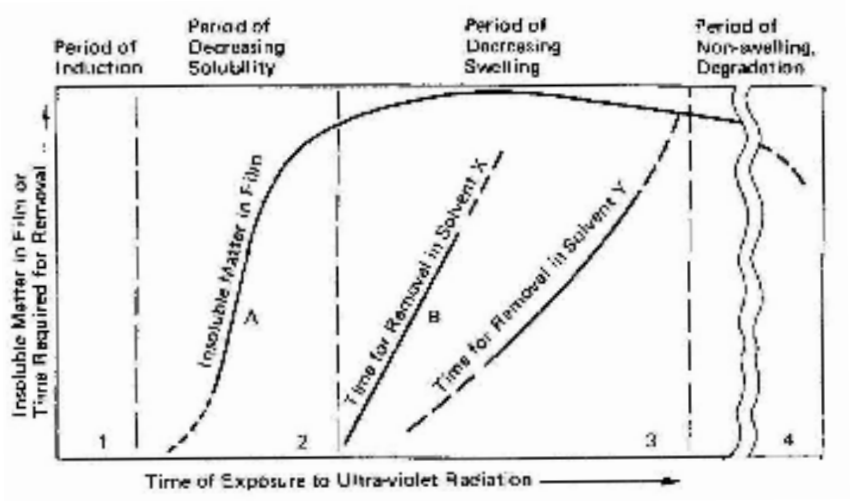


Figure 3. Schematic representation of the stages in the decrease in solubility and swelling in a film of thermoplastic polymer that undergoes crosslinking (3).

showed marked evidence of crosslinking after that period of time; they could be swollen to various degrees and were removable as gels although at times with difficulty. As had been projected for the most advanced stage, solvents were not able to affect the acrylic varnish on one test painting which had been exposed intentionally to especially severe conditions.

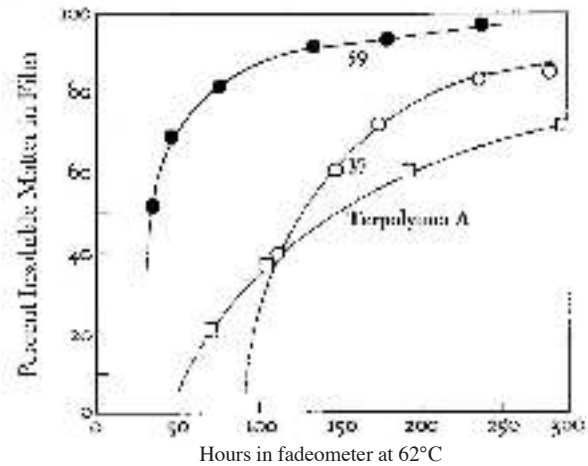
Rise of Insoluble Material

Examples of the rise of insoluble material in three acrylic polymers are [shown] given in Fig. 4: poly(isobutylmethacrylate) (No. 37) and two experimentally-prepared polymers(15). Treatment of these data in terms of the logarithmic fall in the percentage soluble matter, s, plotted against log of the time is shown in Fig. 5, Charlesby's way of looking the change (16) (17). Here, time is expressed in terms of the "gel dose," δ, the time (the exposure) at the first appearance of insoluble matter. When this is done, the behavior of polymers 59 and 37 with respect to crosslinking is seen to be similar, both are tending to become almost completely insoluble. The scale at the right in Fig. 5, an estimate of the ratio of links broken relative to links formed, β/α, can be made conveniently by calculating the fraction of soluble matter, s, present at a time ten times the gel point, according to a simplified version of the Charlesby-Pinner

$$s + \sqrt{s} = \beta/\alpha + 2/\delta.$$

This is the familiar algebraic formula for a straight line, y = a + bx, where y is $s + \sqrt{s}$, a is β/α, b is 2 and x, 1/δ.

Based on this equation, a related method of following the change in solubility is shown in Fig. 6; a plot of $s + \sqrt{s}$ versus 1/δ is used(17). In this case the intercept on the y axis gives the ratio β/α. Depending on the distribution of molecular weights in the particular polymer, the curves for loss of solubility may conform to a family of curves (Fig. 1). Nevertheless, much can often be learned simply by considering the data points to be linear, as seen in the log-log plot of Fig. 7. Here, the ability of various compounds to modify the cross-



Hours in fadeometer at 62°C

Figure 4. Examples of the rise in insoluble matter in three different polymers (15).

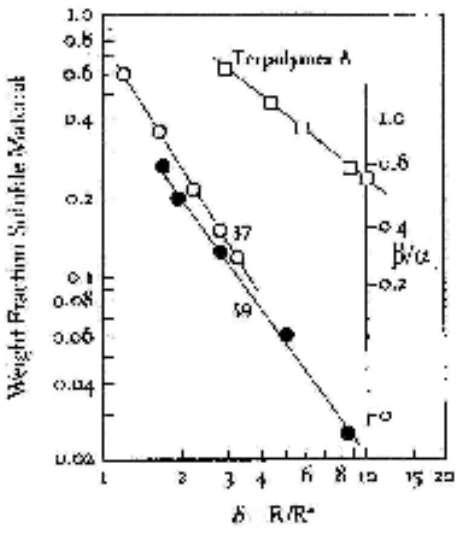


Figure 5. Data of Figure 4 plotted in terms of the fall in the soluble fraction and the gel dose, δ. Scale at left: approximate ratio of chain breaks, ß, to crosslinks formed, α, during fadeometer exposure (15).

linking behavior of Dupont's n-butyl/isobutyl copolymer, Elvacite© 2046 is illustrated: extention of the gel time and the inducement of a degree of chain breaking(18).[5]

The rapid decline leading towards 2% solubility and zero links broken relative to links formed ($\beta/\alpha = 0$) exhibited by polymers 59 and 37 (Figure 5) and by the unihibited Elvacite©2046 (Figure 7) provides the decisive evidence that these polymers will become almost completely insoluble. In contrast, terpolymer A is losing solubility more slowly, undergoing about five breaks for every ten links formed (β/α = ca. 0.55 in Fig.5)(15). Based on the Charlesby-Pinner analysis then, perhaps one could have given the warning to the conservator greater precision by stating that our objective is: "to avoid employing as a surface coating any thermoplastic polymer that tends almost exclusively to undergo crosslinking during accelerated exposure tests."

[5]Ciabach has suggested comparing gel times as a way to evaluate the relative tendency of different polymers to crosslink (19).

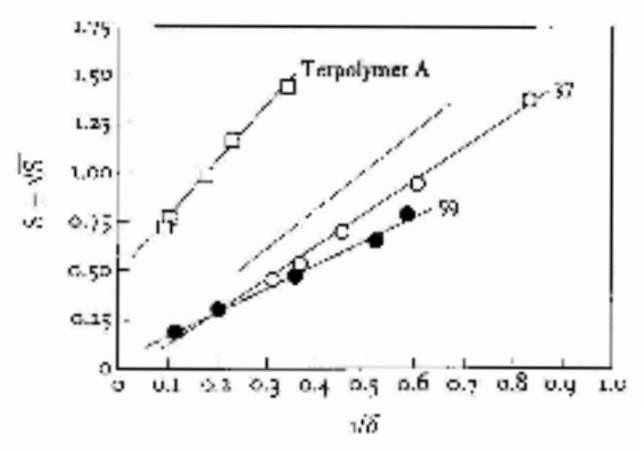


Figure 6. Data of Fig.3 plotted in terms of the Charlesby-Pinner equation, where s = fraction soluble , δ = gel dose (gel time) (15).

Short Wavelength Ultraviolet

In accelerated photochemical aging tests, near ultraviolet wavelengths are often included even though they may not be of major concern in museum practice. The reasoning seems to be that, if a material holds up under the effects of near ultraviolet, it will certainly withstand circumstances encountered in a museum.

Much of the outstanding basic academic research on the photochemical deterioration of acrylics and other polymers, however, has been carried out with mercury-vapor lamps, chiefly at the wavelength of 254nm. It must be kept in mind that different results may be obtained at 254nm in comparison to the action of near ultraviolet and visible wavelengths. Thus, although we have demonstrated that poly(vinylbutyral) will have little tendency to crosslink at the temperatures usually found in museums, a conservator recently remarked that he'd "heard that PVB will crosslink." In this instance, the findings of Mikhailik et al. may have come to his attention; in their work a gel content of 55% had been found when PVB had been exposed to 254nm irradiance at room temperature (20). Ciabach also has reported finding 40% gel at 20°C in PVB that had been exposed under a filter "cutting out the radiation below 290 nm;" perhaps the cutoff needed to be set at a slightly higher wavelength (19). Certainly, when reading research reports on photochemical aging studies, one must check on the wavelengths involved.

Oxidation

During deterioration, a polymer need not undergo extensive chain breaking or crosslinking. As discussed, it may undergo a limited degree of crosslinking. Or it may simply oxidize. The usual result of oxidation is that solvents of increasing polarity tend to be needed to dissolve or swell the material. The low molecular weight resins, AW2, MS2A, dammar, and mastic, are well known to develop the need for more polar solvents during the course of aging, although they have little tendency to develop significant crosslinked material(21). In the case of Acryloid© B82, following an exposure of 2027 hours in a carbon-arc Fadeometer, 62% matter insoluble in toluene was found to have developed; in the polymer emulsion Rhoplex©AC33, 77% (6). Upon extraction with acetone, however, only about 5% insoluble

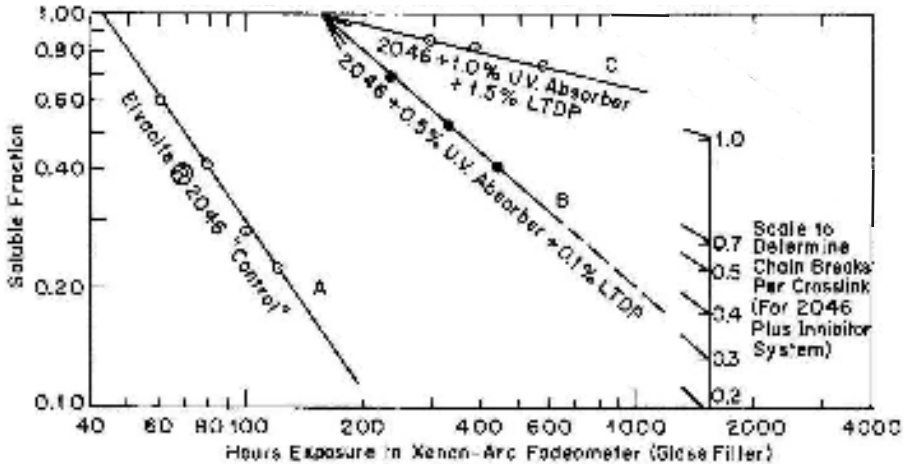


Figure 7. Log-log plot of soluble fraction versus exposure time, showing the effects of various additives on the crosslinking of Dupont n-butyl/isobutyl methacrylate copolymer Elvacite© 2046 (17).

matter was found in either polymer. Apparently the high degree of insolubility in toluene was not due to extensive crosslinking, but to increased polarity in the aged polymers. This and the loss in weight of polymers so often observed to accompany oxidation are aspects of the accelerated aging that warrant future research.

Summary

During photochemical degradation, the formation in some degree of links between the initially separate chains of a thermoplastic polymer is always a possibility to be considered. Such an event, crosslinking, is likely to take place only at a very slow rate under conditions normally encountered in a museum; nonetheless, whenever the application a new type of high molecular weight polymer is under consideration, it is wise to check in advance on the extent to which crosslinking may take place extensively or exclusively.

During photochemical aging tests, the ratio of chain breaking to crosslinking in thermoplastic polymers can be determined on the basis of the Charlesby's analysis of the decline in the soluble fraction. Attention must be given, however, to the temperature of the samples under test; crosslinking is most likely to occur when a polymer is subjected to exposure tests at temperatures above its second order transition temperature.

During the early stages of crosslinking, a thermoplastic polymer coating can often be swollen sufficiently that it can be removed as a gel. Nonetheless, the limit to the degree of swelling and of insolubility that should be tolerated in good conservation practice remains a subject for future research.

The often-heard admonition for conservators to avoid using a particular thermoplastic polymer "because it will crosslink" has primarily been made with reference to the polymers of n-butyl and isobutyl methacrylate and to the experimentally-tested isoamyl variety. Rather than significantly chain breaking, upon aging these have been shown to undergo crosslinking almost exclusively, the property specifically to be avoided.

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