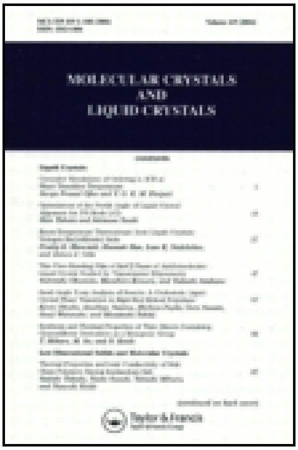

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Plastic Scintillators from Cross-Linked Epoxy Resins†

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Abstract—Several attempts have been made to produce a plastic scintillator based on epoxy resins instead of styrene or vinyl toluene. The advantages of such a system are many. The shrinkage on polymerization would be an order of magnitude less than styrene. Combined with low vapor pressure and a smaller exotherm, this would mean that scintillators could be easily cast into complex and readily reproducible shapes. Since the epoxies are cross-linked systems, such a scintillator would have greater dimensional stability, greater resistance to high temperature and to chemical or solvent attack, and essentially no tendency to stress crack or surface craze. It might be possible to operate such scintillators directly immersed in strong solvents, which could be very advantageous in many chemical and biological experiments. In addition, epoxy resins systems can be easily tailored for special applications by the addition of modifying agents such as flexibilizers.

1. Introduction

The early attempts to make plastic scintillators were based on polystyrene. These attempts were quickly successful and polystyrene and its derivatives, such as methyl styrene[1] and 2,4-dimethyl styrene,[2] remain the base of our plastic scintillators today. The coice of polystyrene is not surprising, as it was one of the first commercially available plastics. Its properties were well known,[3] it was transparent, and it could be produced from a liquid, solvent-free monomer without any reaction by-products. The addition polymerization of a liquid monomer gave a convenient route for the incorporation of scintillator materials into the plastic. They were simply dissolved in the monomer which was then cast into a mold and polymerized into a solid block. Other plastics produced by condensation reactions or from solutions either provided no simple way of incorporating scintillators or no economical method of making large blocks.

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The only other candidate, until quite recently, seemed to be polymethylmethacrylate. It has a liquid monomer, polymerizes through an addition reaction, and is very transparent. However, it is an aliphatic structure in contrast to the aromatic styrene and has been found to be a poor scintillator solvent. It can, however, be made to work by adding an aromatic co-solvent such as naphthalene.[4]

Recent advances in polymer technology have begun to make available other plastics which may be worth examining as scintillator solvents. The most interesting of these seem to be thermosetting materials such as aromatic epoxies, phenyl silicones, aromatic polyesters, and aromatic polyurethanes. A primary difficulty with many of the systems is obtaining material of sufficient transparency, and for this reason, only the epoxy seems to be commercially feasible at present.

2. Advantages

The advantages which may be gained by using an epoxy resin are several. First of all, the system may be easy to cast. Epoxy systems typically shrink only 1 per cent on polymerization, while styrene shrinks about 15 per cent. Thus, the danger of shrinkage cracks is nearly eliminated and mold design is greatly simplified. The components of an epoxy system may be selected to have high boiling points compared to styrene. This means that expensive autoclaves, reflux apparatus, closed high pressure molds, or precisely controllable heating and cooling facilities are not necessary to prevent escape of volatile monomer when casting epoxies. The polymerization exotherm for most epoxies is small enough that castings several inches thick in minimum dimension are easily cast without danger of burn-up. Furthermore, epoxies may be polymerized at room temperature, eliminating the need for ovens or special polymerization equipment of any kind.

Second, the epoxies are two component systems which are quite stable at room temperature without inhibitors. The inhibitors used to stabilize styrene monomer must be removed just before adding the scintillation materials and polymerizing. This stability may make it possible to combine scintillating materials and other modifiers with epoxies to make a two-part liquid system that can be simply stored, then mixed, and cast into solid blocks or shapes as needed.

A third advantage is that the epoxies are thermoset or cross-linked systems, which immediately implies several desirable properties.

Cross-linked plastics are resistant to high temperatures. They will soften but they will not melt. They remain rigid up to their second order glass transition temperatures (perhaps 90°C for a feasible system) and may be usable at considerably higher temperatures in reduced loading.

Cross-linked plastics are dimensionally stable and mechanically strong. They may be machined without warping and will support heavy mechanical loads without creeping.

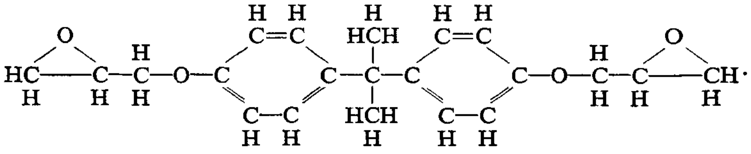
Cross-linked plastics are not subject to crazing, stress cracking, solvent cracking, and such phenomena as are many thermoplastics including polystyrene and its derivatives. Therefore, a scintillator based on an epoxy will not change efficiency with time due to the formation of surface imperfections.

A cross-linked plastic is not soluble. This means that it might be possible to make epoxy based scintillators that can be used directly immersed in strong solvents, although it might be necessary to make special scintillators that could be co-reacted with the epoxy in order to prevent leaching.

It should be mentioned that polystyrene may be made into a cross-linked scintillator system by adding such compounds as vinyl styrene[5] to the monomer. However, the high shrinkage coupled with the early gel of a cross-linked system makes it difficult to produce crack-free castings at significant cross-link concentrations and reasonably large masses.

3. The Resin

The commercially available clear, colorless aromatic epoxy resins are purified diglycidylethers of bisphenol A. The most satisfatory one we have investigated so far is called Epi-Rez 50810 and is made by Jones-Dabney.[6] Its structure is:



This material is a crystalline solid at room temperature (25°C). It will completely melt at 52°C, and upon cooling to 25°C, it remains a supercooled liquid of 4,000–5,000 cps viscosity for a period of several days. It 25 per cent of *p* tert Butyl phenyl glycidyl ether is added to the resin, it will remain liquid indefinitely at 25°C according to Jones-Dabney literature. Early tests were made with Epi-Rez 508, a less pure version of the same resin.

4. Curing Agents

Curing agents for this material may be selected from various anhydrides, amines, sulfides, organic acids, or Lewis acids. Anhydrides such as hexahydrophthalic used with long slow cures may give nearly colorless castings, but they usually yellow if cured on a reasonably short schedule at elevated temperatures. The best materials we have found so far are a cycloaliphatic diamine called C-394[7] manufactured by the Epoxylite Corporation, and two Lewis acids called Epi-Cure 877 and Epi-Cure 8771 manufactured by Jones-Dabney, and only the latter two have produced efficient scintillators.

5. Diluents

In addition to the epoxy resin and curing agent, we must also select a primary solvent, a wave length shifter, a diluent, a flexibilizer, and an antifoam agent, although we have not yet done any work on the latter. The casting of bubble-free scintillators can be quite difficult using a 5,000 centipoise resin, so we first concentrated on finding a suitable diluent. Epoxy diluents can be divided into two broad classes: inert diluents and reactive diluents. The latter have a functionability of one and so do not contribute to either chain extension or cross-linking.

The inert diluents which were tried were naphthalene, xylene, methoxy methyl diphenyloxide (MMDPO),[8] and dibutyl phthalate. Naphthalene was not significantly soluable below its melting point, and so could not be considered for a room temperature curing system. Also we are mainly interested in its possibilities as a secondary solvent, as will be mentioned later. Xylene worked quite well, but its high vapor pressure limits the vacuum that can be used in vacuum debubbling the resin. The methoxy methyl diphenyloxide did not reduce viscosity as well as the xylene and the commercial material had to be distilled to remove yellow color. However, its vapor pressure is low and its tendency to diffuse out must be less than for xylene. The dibutylphthalate was similar to the methoxymethyldiphenyloxide except that it did not reduce viscosity as well. All four diluents could be used with a variety of scintillators in both amine and Lewis acid cured systems.

The reactive diluents tried were epoxy ethyl benzene, dipentene dioxide, and phenylglycidyl ether (PGE). The first two in the Lewis acid cured system caused an immediate high exotherm followed by slow or no cure. In amine cured systems, they might be usable, but there are indications of undesirable reactions from the epoxy ethyl benzene. For example, in a system using epoxy resin, epoxy ethyl benzene, *p* terphenyl (TP), and tetraphenylbutadiene (TPDB), yellowing occurred as soon as the amine C-394 was added. In another similar system, where we tried to replace the TPBD with *p*-bis[2(5-phenyloxazolyl)]benzene (POPOP), yellowing occurred as soon as the POPOP was added (before the C-394 was added). The phenylglycidyl ether worked quite well in all systems. It did not cut viscosity quite as well as xylene, but its low vapor pressure and reactivity made it our choice for the best diluent.

It should be stated that no aliphatic diluents such as allyl glycidyl ether were tried for fear they would reduce the efficiency of the system.

6. Experimental Method

The relative pulse heights (RPH) of different samples were measured by the method of Kaiser and de Villiers.[9] That is to say that each sample was machined and polished into a one-inch diameter cylinder with a standard length of 1 inch. These were greased onto the face of a phototube in a black box and a radioactive source positioned on top of the sample. Pulses from the preamplifier were fed into a linear attenuator in series with a 200 channel analyzer. The attenuator was adjusted for each sample to give the photopeak position at the same channel for all measurements. A 1 inch long by 1 inch diameter piece of "Pilot B" scintillator was used as a standard and all RPH's are reported in per cent of this sample.

7. Secondary Solvents

Naphthalene as a diluent and secondary solvent was tried in a 508 resin system cured with 12 phr[10] of the 877 Lewis acid and using 2 pht[10] of *p*-terphenyl and 0.2 pht of TPBD. It was reasoned that if the epoxy were a poor solvent, there should be an appreciable difference between a scintillator diluted with 20 parts naphthalene and one diluted with 20 parts of phenylglycidyl ether, which is very nearly the same structure as one-half of the symmetrical epoxy molecule. Such an effect would be similar to that reported for naphthalene in polymethylmethacrylate by Brown *et al.*[4] The $\frac{3}{4}$ inch long naphthalene sample gave a relative pulse height of 51 per cent of "Pilot B", and the phenyl glycicyl ether sample, which was $\frac{3}{4}$ inch long, gave 53 per cent of "Pilot B". Since the naphthalene diluted sample was slightly worse, the epoxy resin must be classified as a good solvent.

8. Flexibilizers

Only two flexibilizers have so far been investigated. Both are long chain epoxy terminated aliphatic resins manufactured by Dow Chemical Company. One is DER 732 and the other DER 736. They differ only in molecular weight, with DER 732 having the larger weight. We tried a 508 resin system using 20 phr 732, 12 phr of 877, 2 pht TP and 0.2 pht TPBD. The cured system gave a RPH of 44 per cent in a $\frac{3}{4}$ inch long sample. This compares with 53 per cent for the same system with 20 phr of PGE instead of the 732. This is probably due to the 732's being aliphatic and, therefore, a poor solvent. One would hope that a suitable aromatic flexibilizer might be found but aromaticity and flexibility are usually mutually exclusive. The RPH does not seem to be sensitive to the type of compound used to dilute or flexibilize the resin so long as it is aromatic as seen from the data given in Table 1.

TABLE 1 Effect of diluents

RPH	Resin	Curing agent	Diluent or flexibilizer or solvent	Scintillator	Shifter
51%	508	12 phr 877	20 phr naphthylene	2 pht TP	0.2 pht TPBD
55%	508	12 phr 877	20 phr Xylene	2 pht TP	0.2 pht TPBD
53%	508	12 phr 877	20 phr phenyl glycidyl ether	2 pht TP	0.2 pht TPBD
55%	508	12 phr 877	20 phr MMDPO	2 pht TP	0.2 pht TPBD
44%	508	12 phr 877	20 phr 732	2 pht TP	0.2 pht TPBD

All samples above were only $\frac{3}{4}$ inch long.

9. Optical Properties

The optical properties of the 508 resin cured with the 877 Lewis acid have been investigated by two methods. Figure 1 gives the per cent transmission versus wavelength for a $\frac{1}{4}$ inch thick polished sample of

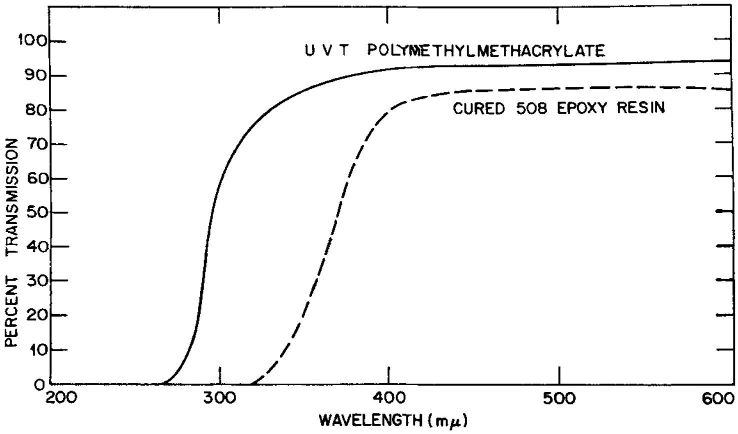


Figure 1. Pulse height versus shifter concentration in liquid epoxy resin.

508 resin-12 phr 877–20 phr PGE as measured with a Cary recording spectrophotometer. The upper curve is the data for a similar piece of ultra violet transmitting polymethylmethacrylate. Figure 2 gives the variation of the RPH with length for the 508 resin-12 phr 877–20 phr PGE-2 pht TP-0.2 pht TPBD. The curve seems to be the sum of two exponentials, as would be expected from the work of Kaiser and de Villiers.[9] The 50810 resin we are now using is purer and so should give better optical properties.

An approximate measurement of the emission spectrum under ultra violet excitation of 508 resin cured with 12 phr of 877 shows a peak at about 3120 angstroms.

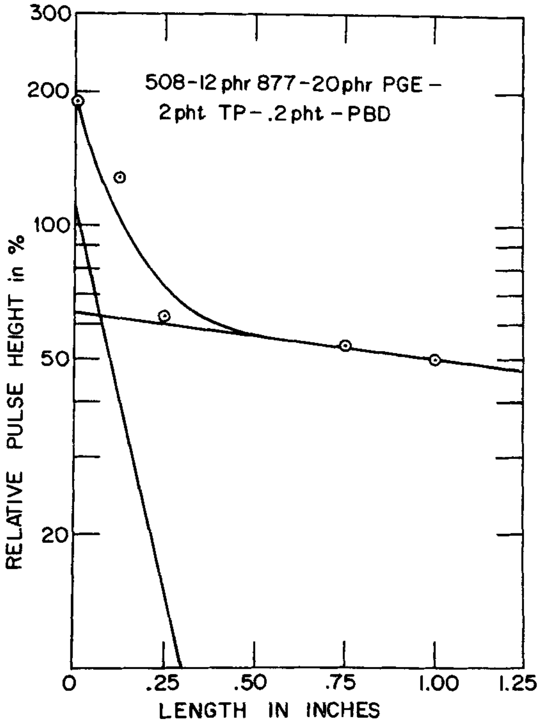


Figure 2. Pulse height versus sample length for an epoxy scintillator.

10. Scintillator Concentration

In order to check the proper concentration of scintillator and shifter in the resin, we ran RPH data versus concentration for 2,5-diphenyloxazole (PPO) in 50810 resin with 20 phr of xylene. The solutions were contained in a thin walled polymethylmethacrylate container 1 inch in diameter by 1 inch tall. PPO was the only good primary scintillator we had that was sufficiently soluble at room temperature to stay in solution during these measurements. The data are presented in Fig. 3. We also ran a similar curve for various concentrations of bisisopropylstyrylbenzene (BPSB) in the same resin and diluent solution with 1 pht of PPO added. The results are shown in Fig. 4. It is probable that in solid solutions of solutes in polymer, higher concentrations can be used without self-quenching.

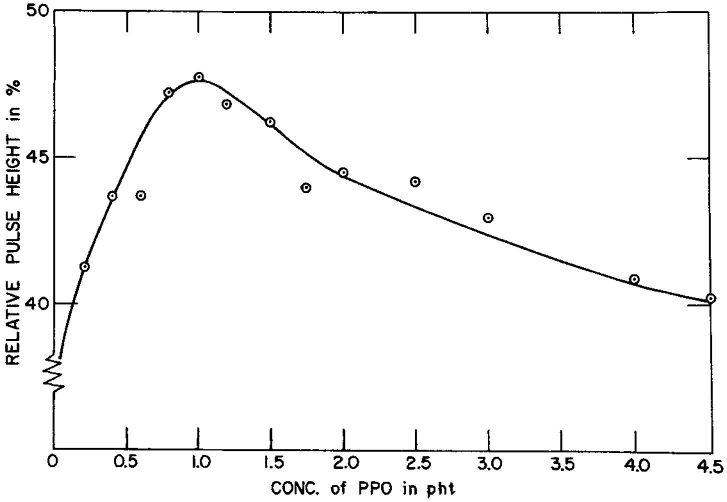


Figure 3. Pulse height versus PPO concentration in liquid epoxy resin.

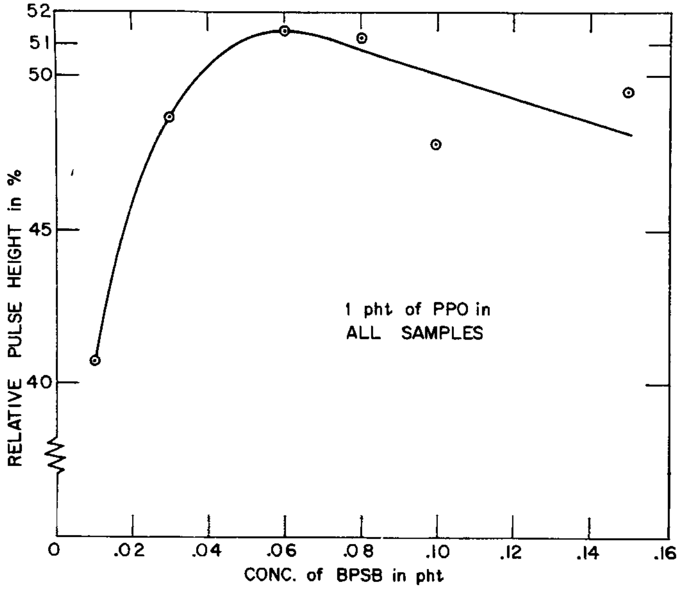


Figure 4. Optical transmission of an epoxy system.

11. Curing agent Quenching

There was the possibility with both amine and Lewis acid curing agents that the curing agent could act as a quencher. The best performance from a 1 inch long liquid sample without curing agent was 51.5 per cent RPH for 50810 resin-20 phr xylene-1 pht PPO-0.06 pht BPSB. The best performance for a cured scintillator $\frac{3}{4}$ inches long was 55 per cent RPH for 508 resin-12 phr 877–20 phr xylene-2 pht TP-0.02 pht TBPD. This would indicate that the 877 Lewis acid did not act as a significant quencher. Nevertheless, we decided to compare several samples using different concentrations of the 877 curing agent. The data is summarized in Table 2. In all cases, the higher RPH is associated with the lower concentration of curing agent.

In the case of the amine system, the results are quite different as can be seen from Table 3 where all samples are 1 inch long. It is estimated that a 1-1/2 inch thick minimum sample dimension is the maximum possible with the amine system. No other scintillator or shifters were tried because most of them would not stay in solution during the cure of the samples. This was due to the lower exotherm of this system and could have been circumvented by using an oven cure. While these results do not say that amine system is impossible, they caused us to concentrate on the Lewis acid cured systems thereafter.

12. Other Scintillators with the Lewis acid

A variety of other scintillators and shifters were tried with the Lewis acid cured system. One problem was immediately apparent and perhaps should have been expected. All materials containing oxazole or oxadiazole groups prevented curing of the epoxy resin by the 877 Lewis acid. If curing at elevated temperatures was tried, yellow or orange compounds were frequently formed. About this time, we obtained a second Lewis acid curing agent called Epi-Cure 8771. It was supposed to be similar to 877 except for a slower cure. This was very desirable since the 877 cured so rapidly that little time was available for debubbling and pouring the material. Also, the 877 is so exothermic that 1 to 1-$\frac{1}{2}$ inches is probably the largest minimum dimension of a casting that could be poured without yellowing or bubbling. The new 8771 Lewis acid proved

TABLE 2 Effect of Lewis acid concentration

RPH	Sample length	Resin	Curing agent	Diluent	Scintillator	Shifter
106%	0.125	508	12 phr 877	20 phr PGE	2 pht TP	0.2 pht TPBD
101.5%	0.125	508	17 phr 877	20 phr PGE	2 pht TP	0.2 pht TPBD
62%	0.250	508	12 phr 877	20 phr PGE	2 pht TP	0.2 pht TPBD
52%	0.250	508	16 phr 877	20 phr PGE	2 pht TP	0.2 pht TPBD
57%	0.750	508	10 phr 877	20 phr naphthylene	2 pht TP	0.2 pht TPBD
51%	0.750	508	12 phr 877	20 phr naphthylene	2 pht TP	0.2 pht TPBD

TABLE 3 RPH of amine cured systems

RPH	Resin	Curing agent	Diluent	Scintillator	Shifter	Color
< 10%	50810	20 phr C-394	20 phr Xylene	1 pht diphenylacetylene (DPAC)	0.08 pht BDSB	none
< 10%	50810	20 phr C-394	20 phr Xylene	1 pht phenylbiphenylyl-oxadiazole (PBD)-	0.08 pht BPSB	none
22%	50810	20 phr C-394	20 phr Xylene	1 pht 2-(1-naphthyl) 5-phenyloxazole (αNPO)	0.08 pht BPSB	none
23%	50810	20 phr C-394	20 phr Xylene	1 pht PPO	0.08 pht BPSB	slight yellow
23%	50810	20 phr C-394	30 phr Xylene	1 pht PPO	0.08 pht BPSB	slight yellow
—	50810	20 phr C-394	40 phr Xylene	1 pht PPO	0.08 pht BPSB	—
Incomplete solution due to lower exotherm caused by large mass of inert diluent.						
20%	50810	20 phr C-394	20 phr PGE	1 pht PPO	0.08 pht BPSB	none
20%	50810	20 phr C-394	30 phr PGE	1 pht PPO	0.08 pht BPSB	none
—	50810	20 phr C-394	20 phr Xylene	1 pht PPO	0.08 pht BPSB	
A 2-$\frac{1}{2}$ inch thick sample which yellowed and bubbled from excess exotherm.						

to react in the same way with the oxazole and oxadiazole containing scintillators, i.e., it would not cure. In addition, the 8771 did not develop enough exothermic heat to keep *p*-terphenyl in solution during cure at room temperature. A few more samples of the 877 system were tried, with variations in the concentration of scintillator and the type of shifter; the results are given in Table 4 where all samples are 1 inch long.

One other scintillator, diphenylacetylene, was tried because of its excellent solubility, but five attempts gave contradictory results and must be repeated.

13. Aging

The 508 sample listed in Table 4 as giving a RPH of only 35 per cent was made with some old 877 and was visibly yellow. Both the epoxy resin and the Lewis acid curing agent will yellow with time, causing poor efficiency in samples made from them. This yellowing may be due to oxidation or photochemical reactions.

TABLE 4 Miscellaneous systems

RPH	Resin	Cruing agent	Diluent	Scintillator	Shifter
54%	50,810	12 pht 877	20 phr Xylene	1 pht TP	0.08 pht BPSB
49%	50,810	12 pht 877	20 phr Xylene	2 pht TP	0.3 pht TPBD
41%	50,810	12 pht 877	20 phr Xylene	0.33 pht TP	0.005 pht TPBD
35%	50,810	12 pht 877	20 phr PGE	2 pht TP	0.2 TPBD

14. Summary

The best 1 inch long sample made so far was the first one listed in Table 4 and gave a RPH of 54 per cent of "Pilot B", which is already better than several commercial plastic scintillators. This pulse height was achieved without *special purification, careful deoxygenation,* or other costly material preparation. Therefore, some pulse height improvement can be expected if more care is taken. However, if no extra purification is done, we can estimate the cost of the materials needed to produce a 54 per cent RPH epoxy scintillator. In large quentities, this would be about 1.23/lb.

In terms of convenience, we have much to achieve. The pot life of the 877 Lewis acid system is too short, and scintillator solubility is too low for a room temperature cure with the 8771 Lewis acid. The viscosity could stand further reduction, and a good defoamer is needed to speed debubbling after mixing. Solubility is too low to make a stable two-part system, so mixing must be done just before use. The scintillator and resin must be heated in order to achieve solution in a reasonable time and then cooled before adding the 877 Lewis acid. Fresh resin and 877 must always be used. These restrictions will prevent the present system from being useful in the average laboratory, but they would not prevent successful mechanized commercial casting of sheet and rod.

15. Future Work

We feel that we have barely begun to investigate this field of new base resins for plastic scintillators, and we plan to continue the work. In the near future, we feel that most effort must be spent in finding a good highly soluble scintillator. We hope that the derivatives of quaterphenyl[11,12] may provide one answer. A soluble scintillator cured with the 8771 Lewis acid may solve most of our problems. Of course, better diluents, flexibilizers, and other additives will be pursued. We may also examine other base resins just to achieve a better understanding of the role of the solvent in plastic scintillators, without considering commerical feasibility.

Acknowledgements

I would like to thank Mr. Thomas Wolsko for making all the samples while working at Argonne as a summer student. I would also like to thank Mr. W. Kaiser for taking care of the relative pulse height measurements for me. My thanks also to Mr. I. Berlman for the ultra violet emission spectra data and Mr. C. Putnam for the transmission spectra data.

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