

Cast Polyacrylonitrile. I. Casting Methods

J. J. PELLON, N. M. SMYTH, R. L. KUGEL, and W. M. THOMAS,
*Central Research Division, American Cyanamid Company,
Stamford, Connecticut*

Synopsis

Clear sheets of polyacrylonitrile are prepared by casting under conditions whereby an adequate supply of monomer is available to the polymerizing mass and process variables are closely controlled. This surprising behavior can be extended to some copolymers of acrylonitrile and to certain other vinyl compounds that polymerize by precipitation of polymer.

INTRODUCTION

If pure acrylonitrile is heated with a trace of catalyst it becomes turbid and then forms a curdy precipitate. By the time half of the monomer has polymerized, the reaction mixture is a hard, coarse white solid.¹ Clear, glassy products had been obtained only by evaporation of solvent from polymer solutions or by molding the granular polymer under heat and pressure. Thus, it was quite unexpected when workers at the Weizmann Institute found that transparent, water-white polyacrylonitrile (PAN) can be obtained by bulk polymerization.^{2,3}

This paper describes the preparation of clear, cast sheets by adaptation of the method originally used in test tubes. Extension of the technique to some copolymers is described, and the behavior of some other heterogeneous systems is discussed. In a second paper we report the physical properties of cast sheets and the effects of various treatments and additives.⁴

When the method discovered in Israel is followed, polymer is allowed to precipitate as usual, and the major portion is converted to a white, chalky mass. The distinguishing feature is that an undisturbed layer of clear monomer is maintained at all times above the solid polymer. As the reaction proceeds, the monomer from this reservoir is drawn into the growing mass of polymer, preventing the formation of voids. Toward the end of the reaction most of the monomer in the solid phase has been converted to polymer, filling the spaces between the original particles with new polymer and thus providing optical homogeneity. At this stage, the mass becomes transparent and appears much like a poly(methyl methacrylate) casting.

CASTING METHODS

Small Castings

Rods were cast simply by allowing monomer to polymerize slowly in a test tube while maintaining a clear upper layer. In a typical experiment, 15 ml. of acrylonitrile containing 0.12 g. *p*-toluene-sulfinic acid and 0.06 g. 30% aqueous H_2O_2 were placed in a test tube. The tube was stoppered lightly and immersed below the level of its contents in a 20°C. bath. Uncatalyzed monomer was added without agitation so as to keep a clear liquid layer above the precipitating mass. Additions were 1 ml. after $1/2$ hr., 3 ml. after $3 1/2$ hr. total, and 5 ml. after $8 1/2$ hr. total. At the end of 3 days, the lower two-thirds of the mixture was transparent and colorless. Granular polymer at the top was discarded. The product could be polished to yield a uniform transparent rod.

This procedure, taken directly from the original disclosure,² could be used for small rods or thin disks. An example is shown in Figure 1. The method could not be used directly, however, to form larger, homogeneous specimens.

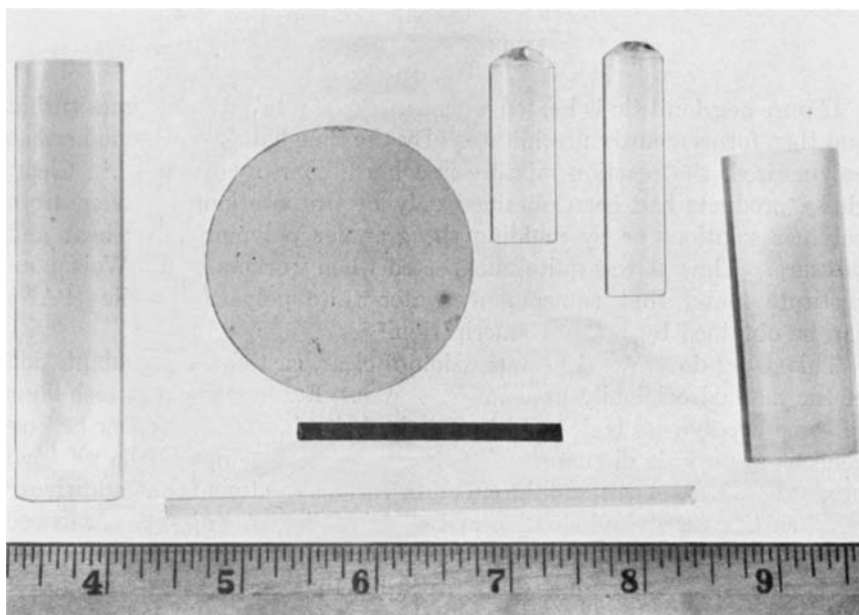
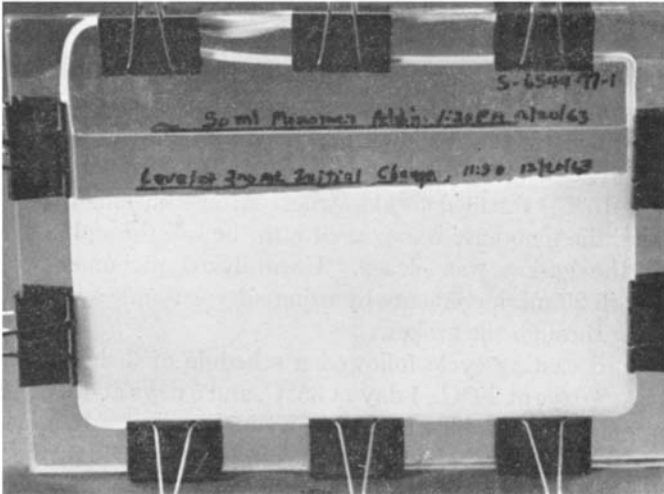


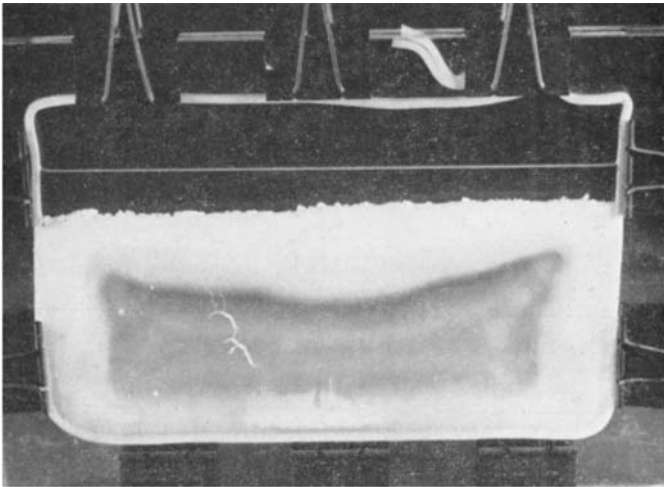
Fig. 1. Rods of PAN cast in test tubes. The flat disk was compression-molded from powdered polymer. Scale in inches.

Cast Sheets

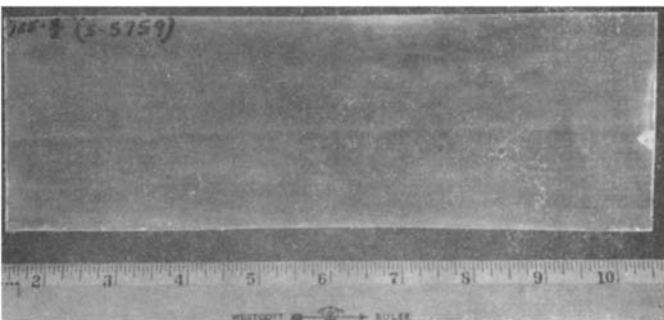
To provide samples for standard physical tests, castings were made in conventional flat 10 × 14 in. cells. Work on this scale was much more difficult and often produced a variety of surface and internal defects.



(a)



(b)



(c)

Fig. 2. Casting in 10 X 14 X 1/4 in. cells: (a) after 2 hr.; (b) after 2 days; (c) after 13 days cure and trimming. Scale in inches,

In a typical experiment, thoroughly cleaned glass plates were assembled into a cell by using a $1/4$ in. poly(vinyl chloride) gasket and spring clamps. Before being filled, the cell was brought to equilibrium in a 20°C . stirred water bath. The starting solution was prepared by adding the catalysts to cooled (10 – 15°C .) distilled acrylonitrile. After solution of the catalysts was complete, the monomer was poured into the cell through a cellophane funnel and the gasket was closed. Uncatalyzed monomer was added subsequently in 20 ml. increments by using a hypodermic syringe with the needle passing through the gasket.

The standard casting cycle followed a schedule of 3 days at 20°C ., 2 days at 23°C ., 2 days at 29°C ., 1 day at 35°C . and 5 days at 40°C .. Changes observed are shown in Tables I and II and in Figure 2. It appears that once a firm cake forms at 30–40% conversion, there is little further shrinkage in thickness of the casting.

In most cases the cast sheet at the end of the cycle contained about 5% monomer. Monomer content could be reduced to less than 0.3% by heating the sheet to 80°C . or above.⁴ A sample of polymer taken from a typical cast sheet was wholly soluble in dimethylformamide, exhibiting an intrinsic viscosity of 3.8 dl./g. (calculated molecular weight 380,000) and a weight-average molecular weight of 543,000 by light scattering.

Fractured surfaces were examined with the electron microscope by T. G. Rochow and M. C. Botty of this laboratory. Photomicrographs

TABLE I
Observations During the Casting Cycle

Time after cell filling, days	Observations
1	Any incipient defects were detectable by differences in cake density when viewed against a light source
2	Start of initial clarification; ca. $1\frac{1}{2} \times 2\frac{1}{2}$ in. opalescent, vertical hour-glass-shaped area in center
4	Complete clarification of initial clearing area.
4–13	Expansion of clear area to ca. $4\frac{1}{2} \times 6\frac{1}{2}$ in.

TABLE II
Monomer Uptake During Casting

Time, hr.	Total monomer uptake, ml.	Overall Conversion, %	Rate of polymerization, %/hr.
5	5	7.6	1.5
22	30	40.8	2.0
47 ^a	52	64.5	1.0
71	62	74.0	0.4
118	70	81.0	0.2

^a The central area of the casting became transparent at this time.

showed rough and smooth areas that perhaps represent the precipitated particles and zones filled by the free monomer.

The *p*-toluenesulfonic acid used in these experiments was prepared from the sodium salt (Eastman) by acidifying an aqueous solution with HCl. The vacuum-dried crystals melted at about 90°C. Catalyst concentrations used in making cast sheets were 10.0 g. *p*-toluenesulfonic acid and 5.0 ml. 30% hydrogen peroxide per liter of acrylonitrile. The acrylonitrile (American Cyanamid Company) was freshly distilled prior to use.

Glass cells thoroughly cleaned with solvents and then with chromic acid cleaning solution gave castings free from defects apparent to the eye. Unfortunately, the polymer could not be parted from the glass. Those release agents tested were ineffective. More satisfactory results were achieved by covering the glass with thin plastic films (Table III). Films were stretched tightly over the glass and secured with tape.

TABLE III

Film	Casting
Mylar polyester	Minor imperfections
Cellulose acetate	Slow polymerization; transparency poor
Polyethylene	Surface irregular and hazy
Polypropylene	Surface poor, film difficult to remove
Teflon fluorocarbon	No defects; lines on Teflon film reproduced on casting
Teflon (coating on glass, not a film)	Some opacity at surface

Some of the difficulties in casting appear to be peculiar to this *p*-toluenesulfonic acid-hydrogen peroxide initiator. Traces of impurities on the glass cell may have induced peroxide decomposition and may have been responsible for gas evolution noted in a few cases. This view is reinforced by the fact that uniform castings were made with azobisisobutyronitrile (AIBN) in place of the standard catalyst.

For use with the azo initiator, the glass plates had been cleaned by soaking in hot Aerosol OT, rinsing with hot water and wiping with a cloth and chloroform. A cell 14 × 20 × ³/₁₀ in. was flushed with argon and filled with monomer containing 3.0 g. AIBN/l. After about 5 hr. in the 30°C. bath the cell was charged with 40 ml. monomer and kept for 6 days at 30°C. without further addition of monomer. The sheet was removed easily from the cell and had no surface defects. The central portion was clear but slightly brown in color. Heating at 80°C. for 18 hr. gave a clear, brown sheet with some opacity and haze at the edges.

Copolymerization

Workers in Israel had noted that certain copolymers could be prepared as clear cast rods. We confirmed this observation in test tube trials by copolymerizing acrylonitrile with 1-15% of a number of common vinyl compounds. These monomers included methyl methacrylate, styrene,

acrylamide, allyl methacrylate, maleic anhydride, ethyl acrylate, vinylidene chloride and ethylene dimethacrylate. Standard sulfinic acid-peroxide initiator was used. Each of these systems presented its special problems, including excessive exotherms, formation of soluble viscous polymer, and general inhomogeneity.

Cast sheets were made successfully from monomer mixtures containing 6 and 12% ethyl acrylate, 6 and 12% methyl methacrylate, and 12% allyl methacrylate. In a typical experiment the cells were assembled from 10 × 14 in. glass plates covered with 0.005-in. Teflon TFE film. Each cell was charged with 200 ml. of catalyzed comonomer mixture and placed in a 20°C. bath. After 4 hr., 60 ml. of uncatalyzed monomer mixture was added. After 60 hr. the castings were transparent and were transferred to a 26°C. bath for 5 hr. At this stage, a slight haze had developed. A small amount of finely dispersed, feathery, birefringent material could be detected with the microscope in most of the copolymer castings.

Monomers Other than Acrylonitrile

The possibility of extending this concept to monomers other than acrylonitrile was obvious to the workers in Israel. Experiments were run with several monomers reported to give opaque products under ordinary bulk conditions.

Vinyl Chloride. When monomer with 0.3% benzoyl peroxide was heated at 40°C. in a sealed tube, the product was a white, opaque solid. These conditions at 50°C. gave an opaque cake, but as reaction progressed, the polymer at the bottom of the tube became transparent. At high conversion, the casting was a brown, transparent plug surmounted by an opaque, chalky coating. A layer of monomer was present above the cake during most of the experiment. Thus, the normal bulk polymerization of vinyl chloride at 50°C. appears to progress through the stages described for acrylonitrile.

Acrylamide. Molten acrylamide (m.p. 85°C.) polymerizes vigorously when a catalyst like di-*tert*-butyl peroxide is present. The product is a glassy foam. Without a catalyst, the monomer polymerized slowly at 85–90°C. The reaction mixture became milky, then opaque and finally transparent. At every stage the polymer appeared to be swollen by monomer.

Methacrolein. A solution of 1% AIBN in monomer was heated at 50°C. The clear liquid became milky, then opaque, and finally nearly transparent. The intermediate opaque polymer appeared to be swollen by monomer.

Vinylidene Chloride. A variety of conditions (0–60°C., six different catalysts) gave only opaque products. These were chalky or chalky at the top and porcelainlike below. A clear monomer layer could not be maintained. The polymer was expected to be crystalline and opacity might have been associated with that fact.

Several copolymers were made in the expectation that they would be amorphous. In each case the reaction mixture comprised 15 parts co-

monomer, 85 parts vinylidene chloride, and 1 part AIBN; it was heated at 40°C. Methyl, ethyl, and butyl acrylates and methyl and allyl methacrylates all produced homogeneous, clear products throughout the copolymerization. Vinyl trifluoroacetate copolymerized heterogeneously to yield a chalk. Styrene copolymerized slowly to a syrup. On the other hand, the copolymer with acrylonitrile behaved in the manner described for acrylonitrile itself. The reaction mixture first formed a cake, which then absorbed monomer from the clear upper layer to give a brown transparent rubber. The mass was cloudy and more rigid near the top and was covered by a white layer of chalk.

DISCUSSION

Work described here fully confirms the concept of preparing clear castings from acrylonitrile.^{2,3} The mechanism appears to be a normal heterogeneous polymerization to perhaps 50% conversion, followed by a stage in which the zones between existing particles are filled with polymer.

Casting with any monomer is a difficult process, increasing in difficulty as the size of the piece increases. All of the normal problems are present in the acrylonitrile case: proper cleaning of the glass, effective release agents, elimination of dissolved gases, and control of the exotherm. The present system has the additional complication that polymer formation must be controlled so closely that monomer can flow freely into all parts of the casting, even at high conversion. Acrylonitrile monomer does not swell the polymer appreciably, and the contraction from monomer to polymer is about one-third. Surface reactions, some of which may be peculiar to the *p*-toluene-sulfinic acid catalyst, complicate the situation further. In view of these problems, acrylonitrile techniques would require extensive development before full-size commercial castings could be achieved.

Copolymers containing at least 85% acrylonitrile often behaved very much like polyacrylonitrile itself. Copolymerization seemed more sensitive to temperature and castings were generally slightly hazy. The haze may have been due in part to marginal compatibility among species with different compositions. Formation of some soluble polymer increased the viscosity of the liquid phase and may have contributed to differences in physical properties of the intermediate cake.

Monomers other than acrylonitrile can form clear castings under appropriate conditions, even though their polymerization is usually described as entirely heterogeneous. Vinyl chloride is an example. In fact, Jenckel and co-workers⁵ have described the polymerization of vinyl chloride under conditions giving a clear yellow lower layer. If the polymer formed is partially crystalline, as with poly(vinylidene chloride), the product may be opaque, even though it has essentially followed the course described for acrylonitrile. In that event copolymerization can prevent crystallization and restore the expected features. Finally, those heterogeneous polymerizations in which the monomer swells the polymer can produce clear

castings without following the pattern of monomer transfer. Extension to nonvinyl polymers was not attempted.

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Résumé

Des films clairs de polyacrylonitrile ont été préparés par coulage dans des conditions dans lesquelles une quantité adéquate de monomère est disponible pour la masse en polymérisation et dans lesquelles les différentes variables du procédé sont contrôlées étroitement. Ce comportement surprenant peut être étendu à certains copolymères d'acrylonitrile et à certains dérivés vinyliques autres qui polymérisent par précipitation des polymères.

Zusammenfassung

Klare Polyacrylnitrilfolien werden unter Bedingungen, welche eine adäquate Nachlieferung von Monomerem zur polymerisierenden Masse und eine enge Kontrolle der Verfahrensvariablen gestatten, hergestellt. Dieses überraschende Verhalten kann auf einige Acrylnitrilcopolymerer und auf gewisse andere, unter Ausfällung des Polymeren polymerisierende Vinylverbindungen ausgedehnt werden.

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