TABLE I
Properties of Typical Vinylidene Chloride–Acrylonitrile
Copolymers

	F-218	F-220
Monomer charging ratio, VC/A	80/20	60/40
Polymerization time, hr.	22	7
Conversion, monomer to polymer, %	49	41
Nitrogen content of polymer, %	6.1	11.2
Acrylonitrile in polymer, wt.-%	23.1	42.4
Intrinsic viscosity in cyclohexanone	0.95	1.87
Intrinsic viscosity in dimethylformamide	0.83	1.84
Permeability of film, cc. (STP)/100 sq. in./ 24 hr./atm./mil		
Nitrogen	0.084	0.422
Oxygen	0.710	3.42
Carbon dioxide	1.77	7.91

Considering experience with other vinylidene chloride-containing films, it is not surprising that these experimental copolymers should exhibit outstanding gas barrier properties. However, such a high degree of impermeability is generally associated with crystalline polymers. For example, the permeability of the amorphous film designated F-218 is of the same order of magnitude as that reported by Dulmage[4] for crystalline Saran film:

	F-218	Saran
Nitrogen (cc./100 sq. in. 124 hr./atm./mil)	0.084	0.11
Oxygen	0.710	0.56
Carbon Dioxide	1.77	2.4

Various researches have emphasized the importance of crystallinity in highly impermeable films. For example, Van Amerongen[5] in his studies of hydrogen permeation through guttapercha, Doty, Aiken, and Mark[6] in their investigation of water vapor permeability of rubber, Morgan's studies[7] of moisture vapor transmission through numerous polymers, Myers and co-workers' studies of the permeability of polyethylenes to gases and vapors[8] and permeability of chlorotrifluoroethylene polymers,[9] and Lasoski and Cobb's study[10] of moisture vapor permeability of polyethylene terephthalate, Nylon 610, and several polyethylenes, have all emphasized the role of crystallinity. Morgan has noted that metal foils, which are highly crystalline materials, are nearly impermeable to water vapor.[7]

Such investigations have not singled out crystallinity as the only factor determining the barrier properties of film-forming materials. However, the importance of this factor in those barrier materials which are crystallizable can easily lead to the generalization that a material must be crystalline to be a good gas or vapor barrier. This is definitely not the case: completely amorphous glass is an excellent gas and vapor barrier. The completely amorphous copolymer films described in this report are also good gas barriers.

It is our belief that studies like the present one will serve to bring the crystallization picture into better perspective. There is ample evidence suggesting that a barrier material will become less permeable as its degree of crystallinity is increased. This finding does not rule out the eventual possibility of a still better barrier that is completely amorphous. Indeed, if a gas barrier depends on crystallinity for its prime property, this may be at the expense of higher density, reduced low-temperature flexibility, and other effects that are also associated with a high degree of crystallinity.

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The Glass Transition Concentration

If a polymer has a glass transition temperature above room temperature, as solvent is removed from a polymer system, a critical concentration region should exist where the concentration of diluent is such that rotation of segments of the polymer molecules starts to be restricted. This should be reflected in the dynamic mechanical properties of the system. A plot of dynamic modulus and damping versus concentration at a fixed temperature should thus have a form analogous to the modulus or damping–temperature plot. This, in fact, proves to be the case.

In measuring the dynamic mechanical properties of solutions, we used the following technique. A fine cotton thread is coated with a polymer solution.[2] While the solvent is evaporating, the dynamic mechanical properties of the supported polymer solution are measured. A free-vibration flexural-pendulum device is used for measuring modulus and damping.[2] In a parallel experiment the rate of solvent evaporation from a polymer-solution-coated cotton thread is measured directly from weight loss. With these data modulus and damping versus concentration curves can be
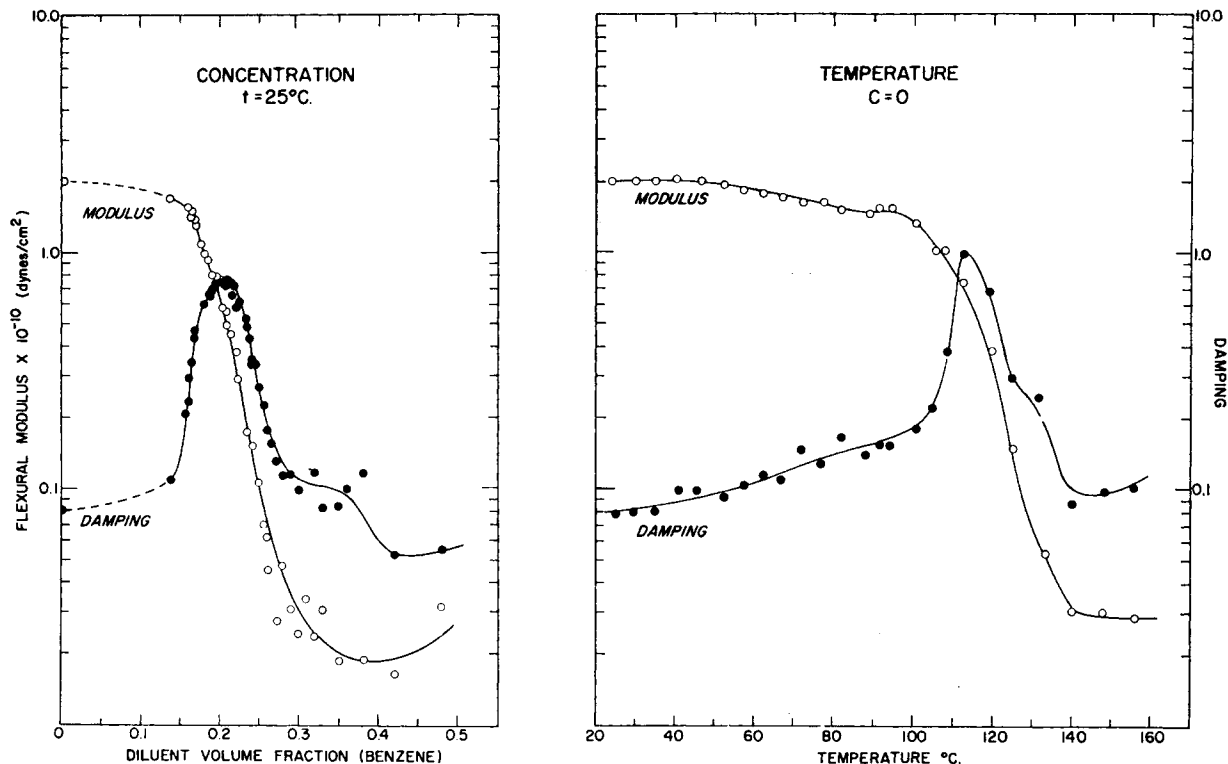
Fig. 1. Dynamic mechanical properties of cotton-filler polystyrene.

constructed. Such plots are found to resemble those of the dynamic mechanical behavior of thermoplastic polymers at various temperatures. For example, a specific solvent concentration range is reached where the modulus curve goes through an inflection while the damping curve passes through a maximum.

By analogy with the glass transition temperature, we call this critical concentration the "glass transition concentration," and give it the symbol Cg. We have made preliminary measurements of polystyrene–benzene, –chloroform, and –ethyl acetate systems, and on poly(methacrylate)–benzene systems. A typical plot is shown in Figure 1. With it, for comparison, is a corresponding plot of dynamic mechanical properties versus temperature. A more complete report, including a discussion of the relation between glass transition concentration and glass transition temperature, will be made later.

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Control of Free-Radical Inhibitor Action in Unsaturated Polyesters

Substituted quinones show quite different relative free-radical inhibitor activities when tested under various polymerization conditions used in unsaturated polyester production and fabrication. In the preparation of unsaturated polyester solutions, such as shown below, it is desirable to produce a solution which is quite stable (does not polymerize) until the material is shaped in a mold. Polymerization should then proceed rapidly to give a solid product which can be removed from the mold. Prior to molding, it is desirable to have a stable solution at elevated temperature (114°C.), such that mixing of high-melting polyesters and vinyl monomers can be done rapidly. A stable solution is also desirable at ambient temperature, so that the solution may be stored prior to use. The advantage of rapid polymerization in the mold is that maximum production from a mold is allowed.
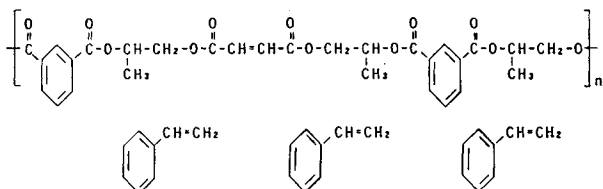
Short polymerization time is usually obtained by means of decomposition of a free-radical initiator such as a peroxide.