

Molecular Weight Enhancement of Vinyl Chloride-Propylene Copolymers

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Synopsis

The chain transfer activity of propylene leads to the formation of vinyl chloride-propylene copolymers with molecular weights lower than those of PVC homopolymers produced under similar conditions. It has been found that the addition of specified quantities of monomers with two or more active double bonds can increase the molecular weight of these copolymers without causing crosslinking.

INTRODUCTION

Vinyl chloride-propylene copolymers have lower melt viscosities than the homopolymer.^{1,2} This gives rise to improved processibility and increased thermal stability.² But, as propylene is a chain transfer agent, the molecular weight of the copolymer is lower than that of the homopolymer prepared under the same conditions, thus limiting the field of application of these copolymers. The work reported here deals with a technique for obtaining practicably higher molecular weight copolymers without detracting from the processibility advantage they have over the homopolymer. This technique is based on the addition of small quantities of molecular weight enhancers which are monomers with two or more active double bonds.

EXPERIMENTAL

Polymerization

The polymerizations were performed in a 1.5 liter glass reactor (Ingenieurbuero SFS, Zurich, Switzerland) using a rectangular blade impeller at 500 rpm and the following recipe: monomers, 330 g; diethyl peroxydicarbonate (laboratory preparation), 0.24 g; Tensaktol A (BASF), 0.1 g; Methocel 90 HG 100 cps (Dow), 0.44 g; $(\text{NH}_4)_2\text{CO}_3$, 0.03 g; water, 560 g. Polymerizations were run at 50°C for 12 hours unless otherwise indicated.

Processibility Measurements

A Brabender Plastograph OHG, Duisberg, Germany, with a Type 30 head was used at 63/42 rpm and a bath temperature of 190°C. The following formulation was used: resin, 34 g; stearic acid, 0.18 g; stabilizer, Mark 292, 1 g.

* Dr. J. A. Waterman passed away on May 2, 1975.

Infrared Spectroscopy

To establish the incorporation of the molecular weight enhancer, the resin was doubly precipitated from a 1% tetrahydrofuran solution using a fivefold volume of hexane and dried in a vacuum oven at 50°C. A 0.25-mm-thick pellet of this material was pressed in a KBr pellet press heated to 120°C. Additive incorporation was confirmed by the appearance of bands characteristic of the material. For example, triallyl cyanurate has bands characteristic of the *s*-triazine ring at 1560 cm⁻¹ and 820 cm⁻¹. For esters, confirmation of incorporation was obtained for materials initiated with lauryl peroxide, The latter in the absence of other carbonyl-containing material gives rise to a barely detectable carbonyl band in the resin, which did not interfere with the detection of ester carbonyl.

RESULTS AND DISCUSSION

Valyi et al.³ have shown that small incremental additions of diisopropenyl-diphenyl to styrene increases the molecular weight of the resulting polymer until a concentration is reached where crosslinking begins and the polymer becomes insoluble. Similar results were reported by Breitenbach⁴ for styrene-*m,m'*-

TABLE I
Effect of Triallyl Cyanurate Feed Concentration on the Intrinsic Viscosity and Gel Content of Vinyl Chloride-Propylene Copolymers

Feed concentration, wt-%		Copolymer		
Propylene ^a	Triallyl cyanurate	Propylene content, wt-% ^b	Intrinsic viscosity, dl/g ^c	Gel content, wt-% ^d
0	0	0	1.02	
6.8	0	4.1	0.63	
6.8	0.03	4.5	0.71	
6.8	0.04	4.1	0.77	
6.8	0.05	4.0	0.81	0.4
6.8	0.06	4.3	0.86	0.4
6.8	0.07	4.1	1.01	2.4
6.8	0.08		1.12	5.9
6.8	0.09		1.05	7.7
6.8	0.10	4.0	0.93	10.3
6.8	0.125		0.83	21.8
6.8	0.15		0.78	26.6
17.3	0		0.43	
17.3	0.06		0.52	
17.3	0.09	7.7	0.60	
17.3	0.10	7.7	0.65	0.4
17.3	0.11	7.4	0.77	1.3
17.3	0.12	7.8	0.74	2.9
17.3	0.13		0.74	8.5
17.3	0.15		0.74	15.5

^a For the low propylene level, conversions ranged from 80% to 85%; for the high propylene level, from 55% to 60%.

^b Determined by density.

^c Concentration corrected for gel content.

^d Determined by the method of ref. 10.

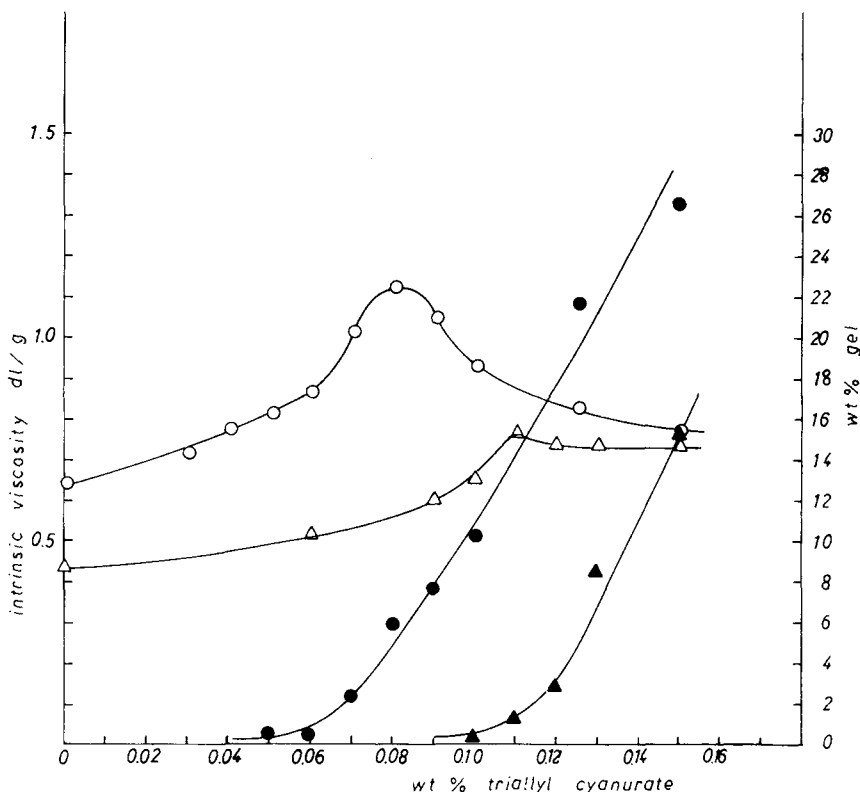


Fig. 1. Intrinsic viscosity and gel content as functions of triallyl cyanurate feed concentration: (O) intrinsic viscosity for 6.8% propylene in feed; (Δ) intrinsic viscosity for 17.3% propylene in feed; (\bullet) gel content for 6.8% propylene in feed; (\blacktriangle) gel content for 17.3% propylene in feed.

divinylazobenzene and styrene-*p*-divinylbenzene systems and by Martin,⁵ who used di- and triallyl esters as well as other unsaturated materials with vinyl chloride. In view of the strong chain transfer effect of propylene, it was not clear a priori whether this molecular weight-enhancing technique could also be applied to the vinyl chloride-propylene system and, if it could, to what extent such an effect could be exploited for practical purposes.

To avoid marked changes in the character of the polymer, the molecular weight enhancer should be effective in low concentrations. The activity of its functional groups should, therefore, be similar to that of the primary monomer. If the activity of these functional groups is much higher than those of the primary monomer, a high degree of crosslinking leading to gel formation will occur at low conversion. If the activity is much lower, the material will be incorporated into the polymer too slowly to be very effective. Valyi et al.³ and Breitenbach⁴ used materials with functional groups very similar to those of the substrate. Most of the materials claimed for PVC contained two or more allyl groups.⁵

The vinyl chloride-propylene system has been found to be amenable to substantial molecular weight enhancement by this technique using materials such as triallyl cyanurate, diallyl adipate, diallyl maleate, allyl methacrylate, and trivinyl cyclohexane.⁶ Of these, the diallyl and triallyl esters were the most

TABLE II
Dynamic Stability and Processibility of Vinyl Chloride-Propylene Copolymers

Poly- merization temp., °C	Diallyl phthalate in feed, wt-%	Polymer propylene content, wt-%	Intrinsic viscosity, dl/g	Brabender data	
				Minimum torque, m-g	Time to degrade, min
45	—	3.7	0.75	1450	20
60	0.15	3.8	0.74	850	44
60	—	3.8	0.55	600	55

suitable materials. Allyl methacrylate is very reactive and renders the system sensitive to gel formation. Trivinyl cyclohexane has a low efficiency.

The effect of increasing concentration of the molecular weight enhancer on the molecular weight and gel content of the copolymer is given in Table I for two propylene levels, using triallyl cyanurate. It will be seen that in the case of the lower propylene level, it is possible to obtain copolymers of intrinsic viscosity as high as that of the homopolymer prepared at the same temperature before unacceptably high gel formation sets in. Figure 1 shows these results graphically. It will be seen that the intrinsic viscosity rises with increasing triallyl cyanurate content until a point is reached where gel appears (crosslinking) after which the intrinsic viscosity begins to fall. The intrinsic viscosity maximum is lower for the copolymer with the higher propylene content. Gel appears suddenly, and its concentration rises sharply with increasing triallyl cyanurate concentration. The amount of triallyl cyanurate tolerated by the system without crosslinking (as judged by the appearance of gel) is higher for the system with the higher propylene content. Under these conditions, the homopolymer tolerates only 0.01% triallyl cyanurate prior to the appearance of gel.

Similar intrinsic viscosity maxima were reported by Cragg and Manson⁷ for emulsion polystyrene to which divinylbenzene had been added. They ascribed the fall of intrinsic viscosity beyond a certain concentration of divinylbenzene to the appearance of microgel. Flory⁸ has explained such effects on the basis of the material of highest molecular weight being selectively involved in gel formation, and, as a result, the average molecular weight of the sol fraction falls.

The molecular weight of the vinylchloride-propylene copolymer can also be raised by lowering the polymerization temperature. However, this increases the melt viscosity, which detracts from processibility and significantly reduces the dynamic thermal stability. A comparison of these two techniques is given in Table II. In one case, an intrinsic viscosity increase from 0.55 to 0.75 dl/g was achieved by reducing the polymerization temperature from 60° to 45°C, while in the second case the same increase was achieved by the addition of 0.15% diallyl phthalate as molecular weight enhancer. The data show that, in the former case, the torque more than doubled while the stability time was cut by 60%. However, when the same intrinsic viscosity increase was achieved with the aid of the molecular weight enhancer, the torque increased by less than half, while the stability time was reduced by only 20%. One possible explanation for this difference in behavior can be based on the assumption of branching produced by the molecular weight enhancer whose incorporation was established by infrared spectroscopy.

The molecular weight enhancers are polyfunctional; and if more than one of the functional groups are involved, as must be the case if molecular weight enhancement takes place, branching must occur. Branching can be expected to reduce interaction between adjacent polymer chains, which can explain the reduction in melt viscosity.

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Received April 1, 1976

Revised May 5, 1976