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## **Polymerization of Vinyl Chloride at Reduced Monomer Accessibility. I. Polymerization at Subsaturation Pressure with Suspension PVC as a Seed**

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### **ABSTRACT**

Vinyl chloride was polymerized at 40-96% of saturation pressure in water suspended systems at 55°C with suspension PVC as a seed. The monomer was continuously charged as vapor from a storage vessel kept at lower temperature. Characterization included molecular weight distribution (MWD) and degree of long-chain branching (LCB) by GPC and viscometry, thermal dehydrochlorination, microscopy, and technical standard tests. A granular seed was necessary to obtain granular polymer and reasonable polymerization rate. In properly seeded systems with monomer-soluble initiator, crust formation is very low. With monomer-soluble initiator the polymerization reactions are restricted to the seed polymer, comprise its total structure, reducing its porosity. At pressure near saturation, molecular weight increased with conversion, and autoacceleration occurred. The changes in molecular weight are presumably due to the lack

of a liquid monomer phase, which reduces the mobility of the radicals leading to decreased termination. At decreasing polymerization pressure the mobility is further reduced due to deswelling of the gel. At low pressure the polymerization rate decreased, the amount of low molecular weight material increased, and considerable long-chain branching occurred as a result of monomer depletion. With water-soluble initiator (at pressure near saturation), new tiny particles were formed in the water phase at the boundary to the seed particles. The seed structure remained unchanged. The polymer formed showed broad MWD and high LCB. No marked reduction in polymerization rate was observed. The dehydrochlorination measurements indicate that the end groups and not the branch points are responsible for the decrease in thermal stability noticed.

## INTRODUCTION

Polymerization of vinyl chloride (VCM) at subsaturation pressure, termed "U-polymerization," is not used in current technical practice. From time to time, however, there has been a considerable patent activity concerning U-polymerization. The main systems discussed are based on monomer-soluble initiators and a granular seed substance, usually S-PVC or M-PVC (PVC obtained by suspension and bulk polymerization, respectively). A liquid suspending medium, such as water, may be used, but "gas-phase" polymerizations are more often discussed. U-polymerization is claimed to give little tendency to crust formation and to be well suited for continuous polymerization processes. The resulting polymer is claimed to have an increased processability and thermal stability.

There are few reports directly related to U-polymerization in the literature. When investigating the kinetics of emulsion polymerization, Ugelstad et al. [1] found a maximum in the rate at about  $P_m/P_m^\circ = 0.87$ , where  $P_m$  is the polymerization pressure and  $P_m^\circ$  is the pressure of saturated VCM at the relevant temperature. The increased polymerization rate was supposed to be an effect of a decrease in the termination rate due to increased viscosity in the PVC particles at the reduced monomer concentration. A reduction in the radical desorption rate might also contribute. Liegeois [2] came to similar conclusions in his study on kinetic models for emulsion polymerization of VCM.

Kahle and Moberly [3] studied gas-phase polymerization of VCM

at  $P_m/P_m^0 \sim 0.9$  using M-PVC as a seed. Initiator productivity was found to be enhanced by the addition of a small amount of hydrocarbon to the system. It was assumed that this was due to improved monomer-to-initiator contact on the surface of the resin particles. With increasing conversion the plasticizer absorption ability of the product was reduced.

Sielfeld and Reichert [4] found gas-phase polymerization of VCM on PVC to take place within the polymer particles, as they are swollen with initiator and monomer. The porosity of the PVC particles decreased with increasing conversion. The polymerization reactions were supposed to be influenced by the high viscosity of the system. There was no autocatalytic effect observed for this system. The polymerization rate was proportional to the initiator concentration and proportional to the square of monomer concentration swelling the PVC particles.

Allsopp [5] found that, when suspension polymerizations of VCM were continued at subsaturation pressure after the pressure drop,  $P_m/P_m^0 = 0.9$ , the smaller pores were filled preferentially with new PVC, and the plasticizer absorption ability of the material was heavily reduced. This was supposed to be due to a higher concentration of precipitated initiator on the walls of the smaller pores, as these pores are the last region in which liquid monomer is expected to persist as the pressure drops.

For radiation-induced VCM polymerization, Russo and Stannett [6] found that  $\bar{M}_n$  decreased and  $\bar{M}_w/\bar{M}_n$  increased at high conversions.

There was also a tendency to an increased degree of long-chain branching (LCB) judged from an increase in the ratio of intrinsic viscosity to sedimentation coefficient. These effects were supposed to be due to monomer depletion rather than to radiation degradation.

For a long period of time, several workers have postulated an increased tendency to different side reactions, e.g., branching at high conversions. In certain cases a reduction in the thermal stability of high conversion material has been noticed and taken as an indication of such side reactions.

In connection with an investigation on the later stages in VCM polymerization we found [7] that U-polymerization presents a simple means of preparing PVC with a substantial and controlled degree of certain abnormal structures such as long-chain branches and broad molecular weight distribution (MWD). In the present paper further work on U-polymerization is reported. It mainly concerns water suspension systems with S-PVC as a seed.

## EXPERIMENTAL

Polymerization

The polymerizations were carried out in stainless steel reactors equipped with stirrers of impeller type. Distilled water was used as suspending medium, S-PVC as a seed, and monomer- or water-soluble peroxides as initiators. These ingredients were charged, and air was removed by evacuation during heating to the polymerization temperature. The top of the reactor was then connected to the top of a reservoir containing liquid VCM at a lower temperature. In this way gaseous VCM was continuously charged to the reactor at a predetermined subsaturation pressure during the polymerization. VCM was of polymerization grade and was obtained from KemaNord AB, Sweden. The amount of U-polymer formed, the conversion, is given as per cent of the amount of seed polymer added. Three different series of polymerization were carried out.

Polymerization Series I. The majority of the polymerizations were carried out in 14-liter reactors with 8 liters water as suspending medium at  $P_m/P_m^\circ = 0.96$  in all polymerizations but two, where  $P_m/P_m^\circ = 0.86$ . As a seed 0.5 or 2 kg of a commercial S-PVC, polymerized at 55°C, was used (Pevikon S 687, KemaNord AB, designated S 687 below). Three different initiators were used: dicetyl peroxydicarbonate (Liladox, KemaNord AB), 2.5 g; dilauroyl peroxide (Laurox, Noury), 5 g; or ammonium peroxydisulfate (persulfate), 10 g. In the polymerizations with Liladox the initiator was charged as a finely dispersed suspension, stabilized by a surface active agent. Different charging routines were applied.

Polymerization Series II. The influence of the seed on the polymerization rate was tested at  $P_m/P_m^\circ = 0.96$  in a 5-liter reactor connected to a glass autoclave, allowing the monomer consumption to be followed. In this case, 3 liters water and 0.89 g Liladox or 4.3 g persulfate were used. For both initiators polymerizations were carried out without and with seed (35 g S 687).

Polymerization Series III. Some polymerizations were performed at  $P_m/P_m^\circ = 0.4$  with a mixture of 0.9 g Liladox and 2.0 g Laurox in a 2.2-liter reactor with 1 liter water [7]. In this case the polymerizations were carried out in two steps. First suspension polymerization was performed at 55°C using 2.0 g methylhydroxypropylcellulose (Methocel 65 HG 50 Cp, Dow Chemical Co.) as a suspending agent. When the pressure drop was reached, the reactor

was connected to a reservoir with liquid VCM kept at 25°C. The S-PVC obtained in the first step thus served as a seed for the following U-polymerization.

### Characterization

The molecular weight distribution (MWD), molecular weight averages ( $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$ ), and LCB were determined by gel permeation chromatography (GPC) and solution viscometry according to Drott's method [8], assuming trifunctional branch points. Details of the GPC analysis and viscometry measurements have been given earlier [9]. No corrections for kinetic energy loss were necessary.

Thermal stability was investigated by two methods, dehydrochlorination and discoloration. The rate of dehydrochlorination of the bulk sample was determined in nitrogen at 190°C [10] and is expressed as HCl evolved (in per cent of the theoretical amount) per minute. During the discoloration test, film samples were kept at 180°C in a heated press. After different time intervals the reflectance was measured at 450 nm, MgCO<sub>3</sub> being used as a standard for 100 per cent reflectance [11].

The particle structure was investigated by light and electron microscopy. The porosity was determined with a Hg penetrometer (Aminco Porosimeter 5-7118) as a percentage of the total particle volume [11]. The bulk density was measured according to ISO/R 60. The particle size distribution was obtained by sieving [11]. A Brabender Plastograph was used to determine the time to gelation and melt viscosity [11].

## RESULTS AND DISCUSSION

### Use of a Seed Substance

The influence of the seed on polymerization was tested in polymerization series II. To judge from the negligible monomer consumption, the polymerization rate was practically zero if no seed polymer was used in U-polymerizations with a water-soluble initiator (Fig. 1). Traces of crusts were formed on the reactor walls at the water surface.

With a monomer-soluble initiator, the monomer consumption was measurable, but the polymerization rate was still very low (Fig. 1). No granular polymer was formed. Instead, solid crusts slowly developed on the reactor walls and on the stirrer. If the amount of seed

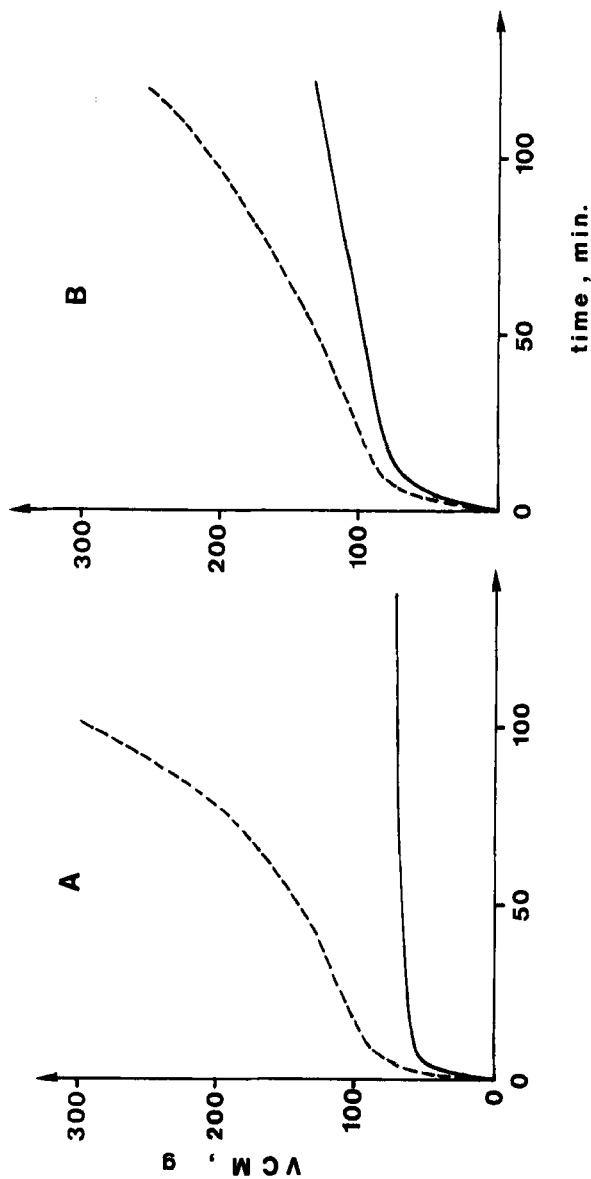


FIG. 1. Influence of seed on the polymerization rate at  $p_m^0/p_m^o = 0.96$ : (A) water-soluble initiator; (B) monomer soluble initiator; (—) without seed; (---) with 35 g seed. The initial monomer consumption is due to the filling of the reactor.

was below a certain level, the particles aggregated and (spherical) crusts were formed. With sufficient amount of seed no aggregation occurred and no crusts developed on the reactor walls. The polymerization proceeded with "normal" rate and showed autoacceleration, (Fig. 1). An increase from 0.5 to 2.0 kg of seed in polymerization series I increased the overall rate about 50% (Table 1).

Although the organic peroxide used was finely dispersed and water-insoluble, it did not act properly as a seed. Possibly, the initiator particles became sticky after monomer absorption and deposited on available surfaces of the reactor. The reactive zone thus created should be highly concentrated, small in area, accessible from one side only and should be quickly covered by a polymer layer of a rather dense structure. These factors should contribute to the low polymerization rate observed.

Obviously, a minimum amount of granular seed substance is necessary in order to obtain a granular polymer product and a reasonable polymerization rate. When water-insoluble initiators, are used, the seed functions as a carrier for the initiator, increasing the area and accessibility of the radical producing zone. However, if the evidence from the series with water soluble initiator is also taken into account (see below) it is obvious that the main function of the seed is to act as a monomer absorbing agent, increasing the monomer concentration in regions of high radical activity. In either case the seed particles provide granular nuclei for the polymerization.

Of course, the seed particles must not aggregate after monomer absorption. For obvious reasons, granular (and porous) PVC is a convenient seed substance. The PVC formed will in any case be the dominating seed already after a fairly low degree of conversion. In a properly seeded U-polymerization system with monomer-soluble initiator there should be no tendency to crust formation. In this respect U-polymerizations seem to have a definite advantage over conventional suspension polymerizations.

### Monomer-Soluble Initiator

Different ways of adding the initiator were tested. No marked influence on the polymerization rate, molecular structure and morphology was observed (Table 1). In all U-polymerizations using monomer-soluble initiators the particle size increased and the porosity decreased with conversion (Fig. 2 and 3).

Morphology and Locus of Polymerization. The particle size distribution and the microscopic investigations show that



TABLE 1. Polymerization Series I: Polymerization Data, Molecular Weight Averages, and Long-Chain Branching

No.	Type	Initiator		Time (hr)	Conversion (%) of seed)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_z \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_n$	LCB/1000 C
		Charging									
S 687	-	-	-	-	-	50	112	219	2.2	2.2	0.4
1	Liladox	After heating		3.5	300	48	127	318	2.6	2.6	0.7
2	"	to 55°C		5.2	680	58	143	349	2.5	2.5	0.6
3	"	Before heating		5.8	420	51	132	336	2.6	2.6	0.6
4	"	"		6.0	620	58	147	362	2.5	2.5	0.7
5	"	In five portions during polymerization		5.3	390	52	136	362	2.6	2.6	0.6
6	"	"		8.0	700	55	142	371	2.6	2.6	0.9
7 <sup>a</sup>	"	After heating		4.5	300	48	124	303	2.6	2.6	0.7
8 <sup>a</sup>	"	"		8.4	500	51	137	356	2.7	2.7	0.8
9 <sup>b</sup>	"	"		2.0	60	50	124	280	2.5	2.5	0.7
10 <sup>b</sup>	"	"		2.4	80	53	121	259	2.3	2.3	0.5
11	Laurox	"		4.5	600	51	128	278	2.5	2.5	0.4
12	"	"		4.7	630	56	137	316	2.4	2.4	0.6
13	Persulfate	"		8.0	530	39	114	300	2.9	2.9	1.3
14	"	"		8.2	700	38	122	402	3.2	3.2	3.1

<sup>a</sup> $P_m/P_m^0 = 0.86$ , all other polymerizations  $P_m/P_m^0 = 0.96$ .

<sup>b</sup>Increased amount of seed (2 kg instead of 0.5 kg).

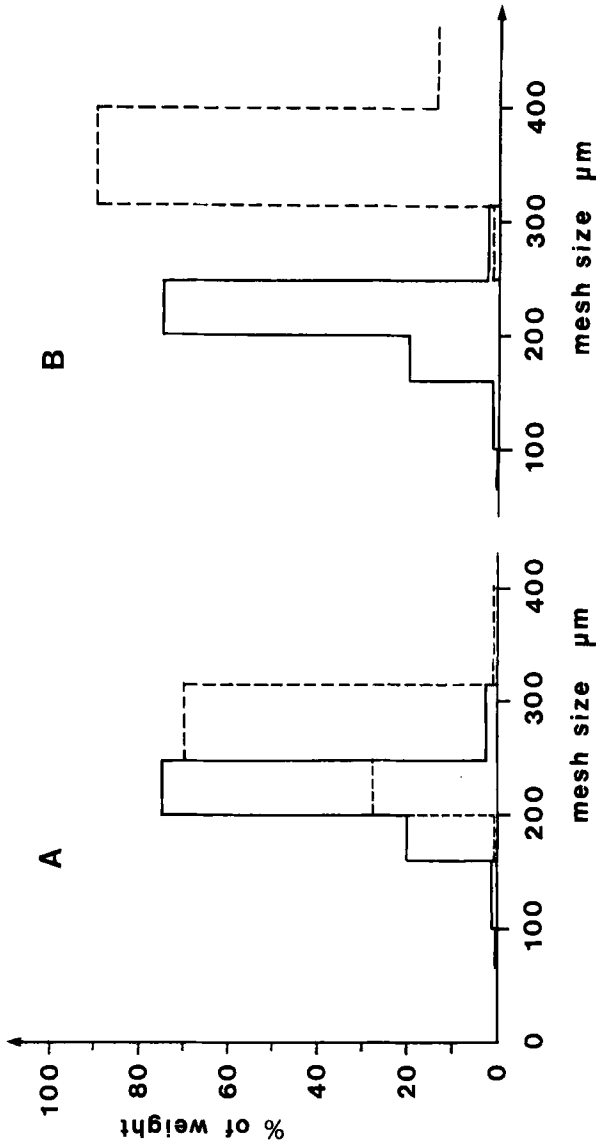


FIG. 2. Changes in particle size distribution with conversion at  $P_m/P_m^0 = 0.96$ , monomer-soluble initiator: (—) seed; (---) 80% conversion, (B) (---) 700% conversion.

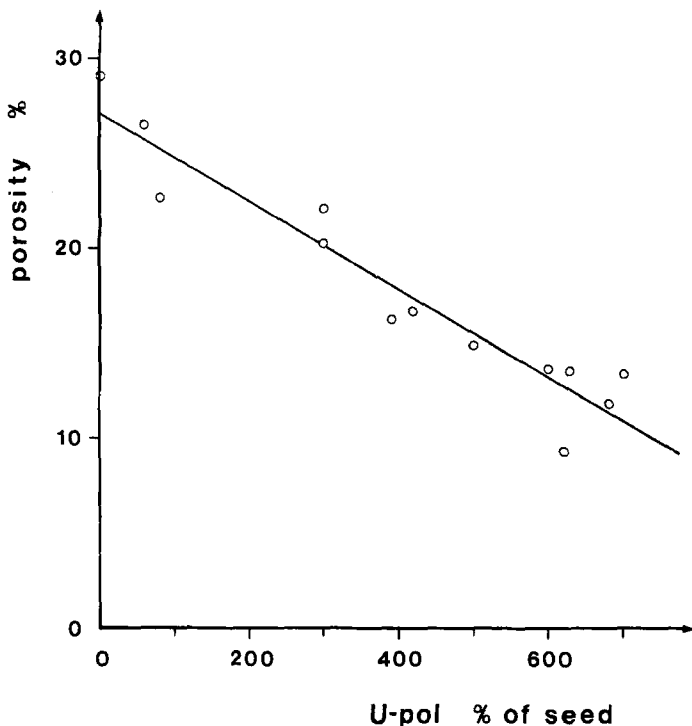


FIG. 3. Changes in porosity with conversion at  $P_m/P_m^0 = 0.96$ , monomer-soluble initiator.

no new particles were formed. Instead, the existing polymer phase was enlarged (Figs. 2 and 4). A closer inspection (Figs. 5 and 6) indicates that the polymer formed has a dense and uniform structure and that the U-polymerization involved all parts of the seed. This suggests radical activity in regions of the seed not directly accessible to the initiator suspension. This must be due to the lack of a liquid monomer phase. At the start of the polymerization process the total amount of the initiator is deposited on the surface of the seed particles. The initiator concentration in the surface layer will be quite high and there should be a strong tendency for the initiator molecules and the oligomeric radicals formed to diffuse into the monomer swollen gel. This not only extends the polymerization reactions to all parts of the seed structure but also result in a

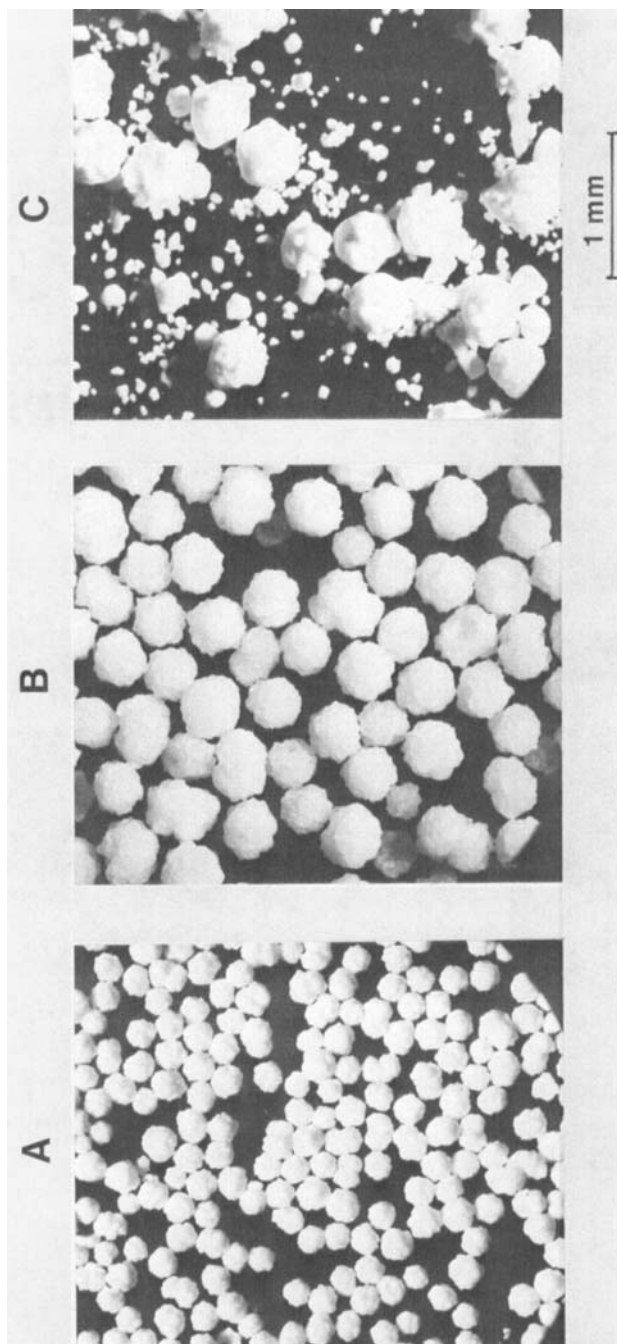


FIG. 4. Influence of initiator type on particle size at  $P_m/P_m^0 = 0.96$ ; (A) seed; (B) monomer-soluble initiator, 680% conversion; (C) water-soluble initiator, 700% conversion.

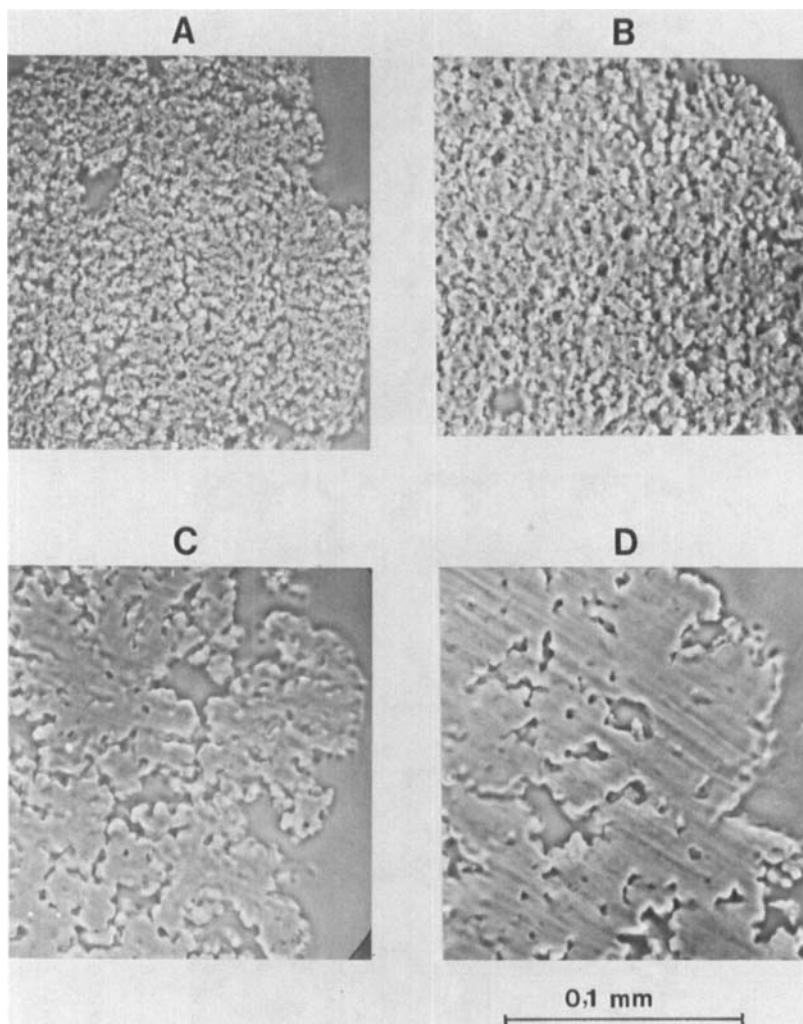


FIG. 5. Changes in morphology with conversion at  $P_m/P_m^0 = 0.96$ , monomer soluble initiator: (A) seed; (B) 60% conversion; (C) 420% conversion; (D) 680% conversion. Light microscopy.

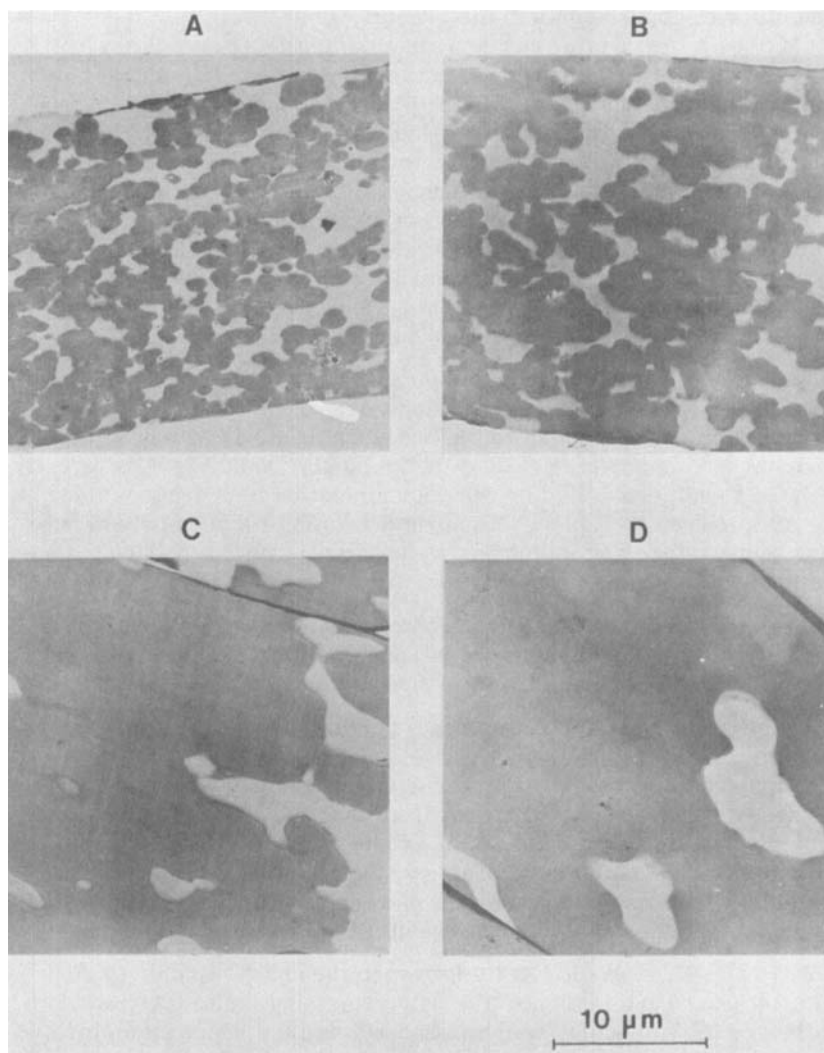


FIG. 6. Changes in morphology with conversion at  $P_m/P_m^0 = 0.96$ , monomer-soluble initiator: (A) seed; (B) 60% conversion; (C) 420% conversion; (D) 680% conversion. Electron microscopy.

decreased porosity. Presumably, a gradual increase in polymer density with conversion will also occur.

Molecular Structure and the Course of Polymerization. Next to propagation, chain transfer to monomer is the dominating reaction in ordinary VCM polymerizations. More than 80% of the chain growth is stopped by chain transfer to monomer. The remaining macroradicals are terminated by mobile radicals [12]. The high transfer to monomer accounts for the narrow MWDs observed [6]. The transfer to polymer is very low leading to negligible long-chain branching. LCB values of 1/1000 C and 0.5/1000 C have been reported for commercial PVC qualities by NMR [13] and GPC/viscometry [9] measurements, respectively. Judging from measurements on  $\overline{M}_w/\overline{M}_n$ , LCB should be less than 0.1/1000 C [14].

Another effect of the high chain transfer to monomer is the fact that the molecular weight is nearly independent of the initiator concentration and the conversion up to the pressure drop. In ordinary bulk and suspension polymerization, the molecular weight is thus directly related to and controlled by the polymerization temperature alone [6].

As is shown in Table 1, the normal relation between polymerization temperature and molecular weight is not obeyed in U-polymerizations with monomer-soluble initiator at  $P_m/P_m^\circ = 0.96$ . The molecular weight increases with conversion due to an increased formation of high molecular weight species (Fig. 7). At conversions of 600-700%, this results in  $\overline{M}_w$  values which are 30-40% higher than for a conventional S-PVC (the seed) polymerized at the same temperature.

Obviously, in these U-polymerizations the course of the polymerization reactions was different from that operating in normal bulk and suspension polymerization of VCM. As shown by the small changes in the LCB value in Table 1, the increase in molecular weight was not due to any marked increase in the chain transfer to polymer. At  $P_m/P_m^\circ = 0.96$  the solubility of VCM is reduced by 15% only [15]. This should hardly influence the chain transfer to monomer either. Termination is the only remaining factor which will influence the molecular weight. Consequently, a decrease in termination should be the major reason for the abnormally high and increasing molecular weight observed and also contribute to the auto-acceleration mentioned above. The decrease in termination must, in its turn, be an effect of reduced mobility of the oligoradicals and of a restricted segmental movement of the trapped macroradicals.

It has been proposed that the higher viscosity of the partly de-swollen gel at subsaturation pressure is likely to reduce termination

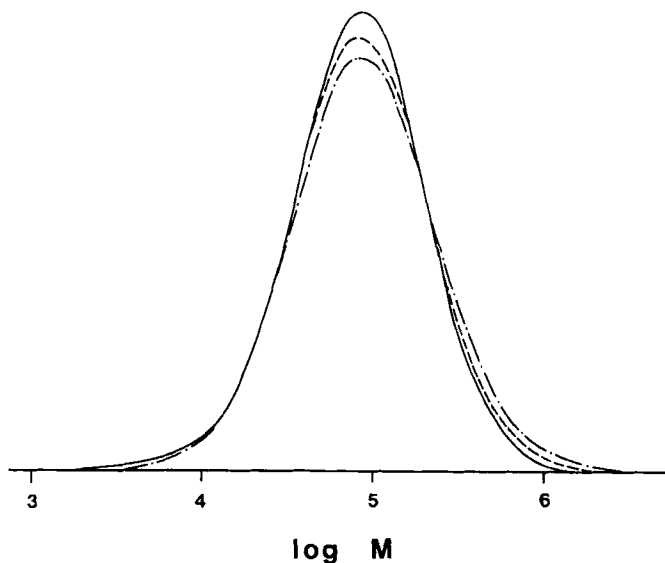


FIG. 7. Changes in MWD with conversion at  $P_m/P_m^\circ = 0.96$ , monomer-soluble initiator: (—) seed; (--) 80% conversion; (- · -) 620% conversion.

[1, 2]. However, at  $P_m/P_m^\circ = 0.96$ , the small reduction in VCM solubility should result in minor viscosity changes only. Another factor which should affect the termination is the absence of a liquid monomer phase in contact with the reactive zone. There will thus be a great reduction in diffusion over the phase boundary and no easy access that way for the mobile radicals to terminate trapped macroradicals in the surface region. Furthermore, as mentioned above, it is likely that the lack of monomer phase will create a more dense structure of the reactive region than in ordinary VCM polymerization, where the surface layer is formed by precipitating molecular aggregates and macroradicals with high segmental mobility. This would also contribute to the increase in molecular weight observed. The auto-acceleration might be influenced by the increasing amount of seed in the system.

The "Max Effect." Even just below saturation pressure, the polymerization rate should be increased due to the absence of a liquid



monomer layer. Further decrease in pressure will result in deswelling of the gel leading to higher viscosity. This should decrease termination and lead to increased polymerization rate as long as there is no monomer depletion. The "max effect" reported by Ugelstad et al. [1] for U-polymerization in an emulsion system is in accordance with this. They found that the polymerization rate increased considerably with decreasing pressure to  $P_m/P_m^\circ = 0.87$  and then decreased. At  $P_m/P_m^\circ = 0.75$  it was still about twice the rate for normal polymerization. The rate then rapidly dropped. We did not notice such effects in the polymerization system investigated in this work. When reducing the pressure from  $P_m/P_m^\circ = 0.96$  to  $P_m/P_m^\circ = 0.86$ , the overall rate was somewhat reduced and at  $P_m/P_m^\circ = 0.75$  markedly reduced. There might have been a maximum in rate but not as pronounced and/or extended as in the experiments reported by Ugelstad et al. The lack of emulsifier and the different initiating system and surface area of the seed in our polymerizations might be responsible for the difference in behavior.

Long-Chain Branching. When the polymerization pressure is sufficiently reduced, the effect of monomer depletion will influence the reaction course. In polymerization at  $P_m/P_m^\circ = 0.4$  with monomer soluble initiators [7] the rate was very low. A considerable broadening of the MWD occurred due to an increase in both high and low molecular weight material (Fig. 8 and Table 2). As shown by Fig. 9 an extensive long chain branching occurred.

At  $P_m/P_m^\circ = 0.4$  the solubility of VCM in water and PVC is only 25% and 15%, respectively, of the solubility at saturation pressure [15]. The reduced monomer concentration should result in a reduced chain transfer to monomer and also to a reduced rate of propagation, resulting in lower overall rate of polymerization. As the rate of initiator decomposition will not decrease with deswelling of the gel, the concentration of mobile oligomeric radicals will increase. The increased radical concentration and the reduced mobility in the deswollen gel should increase the tendency to mutual termination of oligoradicals, thus increasing the content of low molecular weight polymer. On the other hand, the increased immobilization will, per se, contribute to a reduced termination of macroradicals and increase the possibility of formation of high molecular weight material. The dense structure of the gel will also enhance reactions between radicals and polymer molecules, leading to long-chain branching.

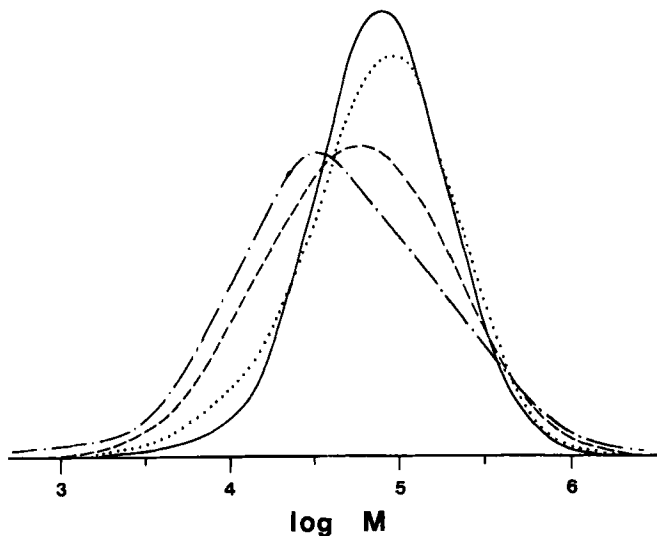


FIG. 8. Changes in MWD with conversion at  $P_m/P_m^\circ = 0.4$ , monomer-soluble initiator: (—) seed; (· · ·) 10% conversion; (--) 30% conversion; (- · -) 80% conversion.

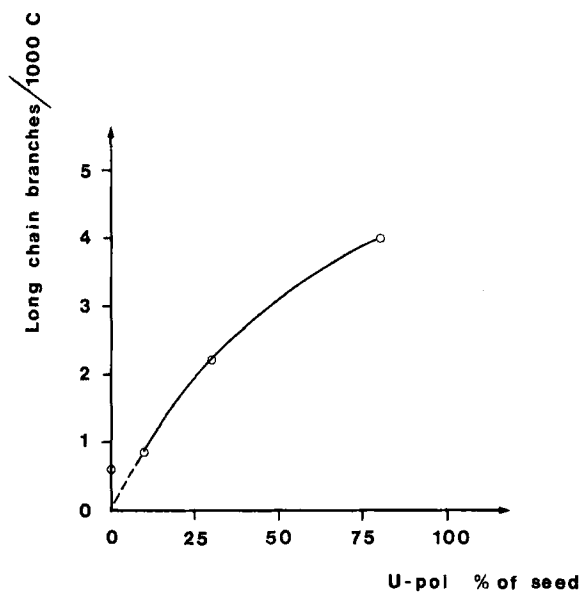


FIG. 9. Changes in LCB with conversion at  $P_m/P_m^\circ = 0.4$ , monomer-soluble initiator.

TABLE 2. Polymerization Series III: Molecular Weight Averages, Long-Chain Branching, and Thermal Stability

No.	Conversion (% of seed)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_z \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	LCB/ 1000 C	Rate of dehydrochlorination (%/min $\times 10^2$ )
1	seed	49	114	233	2.3	0.6	1.0
2	10	39	117	265	3.0	0.9	1.9
3	30	25	109	347	4.4	2.2	4.4
4	80	16	102	522	6.4	4.0	12.1

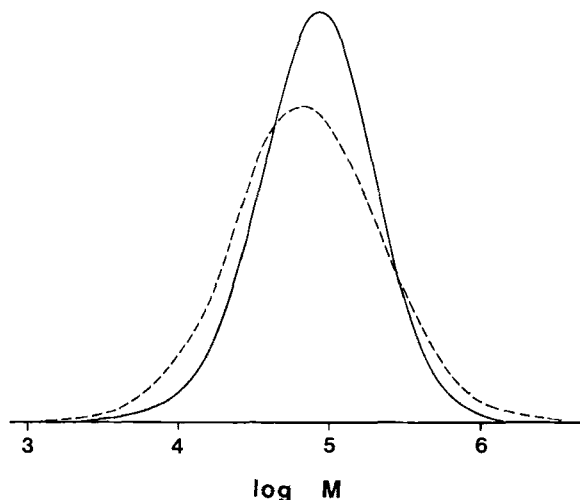


FIG. 10. Changes in MWD with conversion at  $P_m/P_m^\circ = 0.96$ , water soluble initiator; (—) seed; (--) 700% conversion.

#### Water-Soluble Initiator

In order to test the possibility of achieving a substantial LCB even at  $P_m/P_m^\circ \sim 1$ , polymerizations were carried out with water soluble initiator at  $P_m/P_m^\circ = 0.96$ . It was assumed that initiation should occur in the water phase, where the accessibility of monomer would be low.

As is shown by Table 1 and Fig. 10, these reaction conditions resulted in polymers with a molecular structure similar to that obtained at  $P_m/P_m^\circ = 0.4$  with monomer-soluble initiator. The LCB values were quite high and the MWD broad, containing both lower and higher molecular weight species than those in the seed polymer. Favorably enough, the rate of polymerization was much higher, being similar to that obtained at  $P_m/P_m^\circ = 0.96$  with monomer-soluble initiator.

The microphotographs show that the U-polymerizations with water-soluble initiator resulted in a morphology completely different from that obtained with monomer-soluble initiator (Figs. 4 and 11). New tiny particles were formed and were loosely aggregated round the seed particles. No change in the structure of the seed was observed.

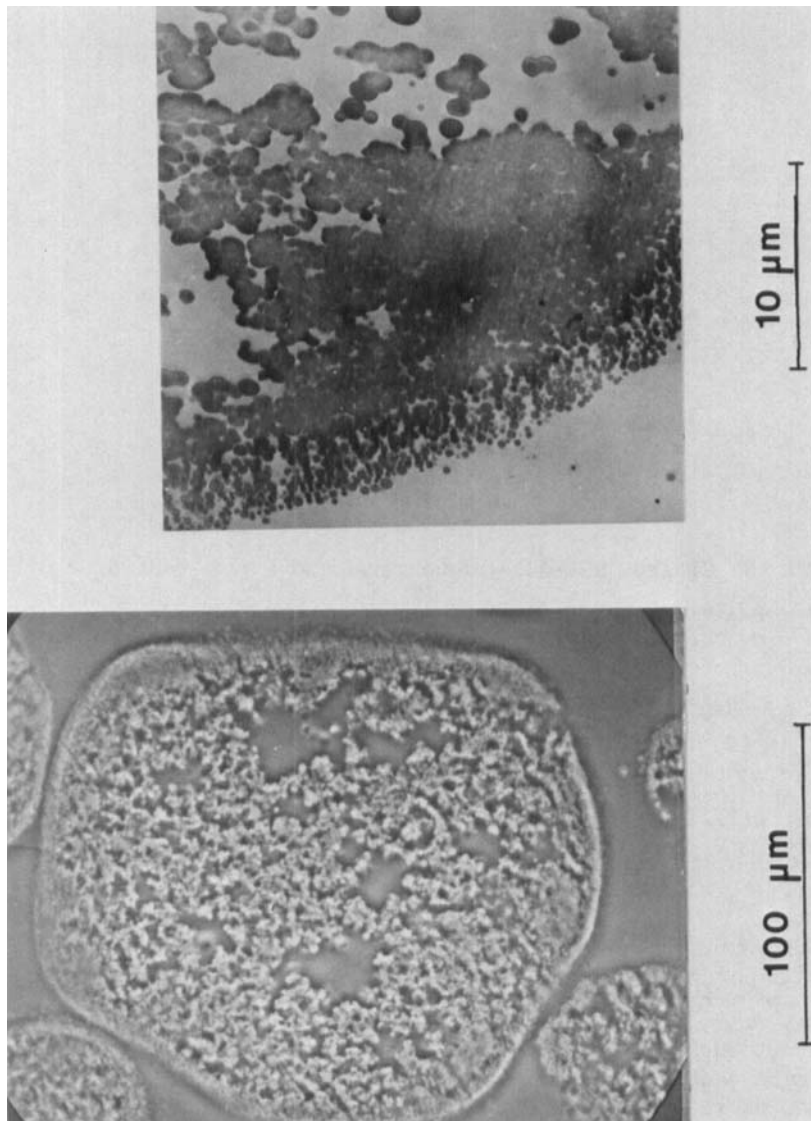


FIG. 11. Morphology of U-polymerizates with water-soluble initiator;  $P_m/P_m^0 = 0.96$ ; 530% conversion; light and electron microscopy.

As mentioned above, no polymerization occurred in the absence of seed polymer apart from traces of crusts formed on the reactor walls at the water surface. Apparently, when water-soluble initiators are used, the polymerization takes place in the water phase at the boundary to the monomer-swollen polymer phase where the availability of the monomer is higher than in the bulk of the water phase. However, as indicated by the MWD and LCB values obtained, the monomer starvation at the reaction zone is much more pronounced than when monomer-soluble initiators are used at the same pressure. The autoacceleration observed is due to the increase in the area of the polymer-water interface.

The reason why the new particles retained their identity and were not built into the seed particle structure might be similar to that governing the formation of particles in ordinary VCM polymerizations. The small size of the new particles might reflect the low solubility of the growing polyradicals in the water. Possibly, the presence of sulfate end groups contributed to the stabilization of the suspension by reducing the hydrophobic character of the particle surface.

The loosely bound aggregates resulted in a considerable increase in the mean particle size, as well as in irregular structure and formation of fines (Figs. 4 and 12). As mentioned above, the porosity of the seed particles was retained. The interstitial volume between the new particles resulted in a porosity for the aggregates exceeding the measuring range of the standard Hg penetrometer used (45%).

When a mixture of water-soluble and monomer-soluble initiators was used at  $P_m/P_m^\circ = 0.96$ , the rate of polymerization and the structure of the polymer was intermediate between that obtained with the respective initiators alone (Fig. 13).

### Thermal Stability

In patents concerning U-polymerization, improved thermal stability is claimed. The polymerization conditions usually comprise a monomer-soluble initiator and  $P_m/P_m^\circ$  close to unity. When monomer soluble initiators were used in our experiments, some of the U-polymers prepared at  $P_m/P_m^\circ = 0.96$  showed a pronounced decrease in thermal stability compared to the seed (Table 3). This inferior behavior was traced to the suspending agent used in the initiator suspension. Products of other U-polymerizations at  $P_m/P_m^\circ = 0.96$  showed properties slightly better than those of the seed.

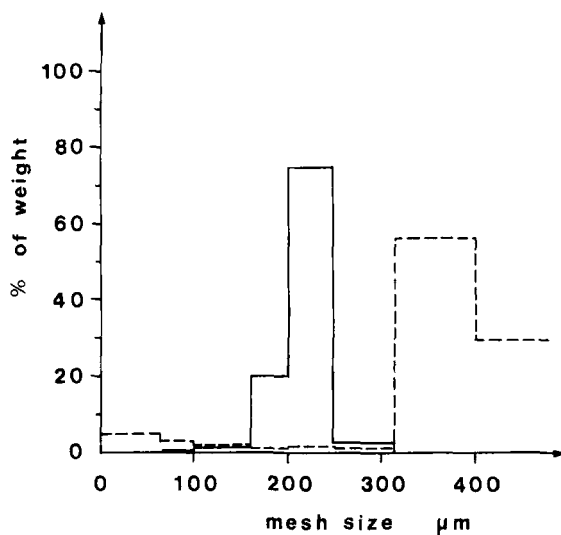


FIG. 12. Particle size distribution of U-polymerizates with water-soluble initiator at  $P_m/P_m^\circ = 0.96$ : (—) seed; (--) 700% conversion.

In the above polymerizations at  $P_m/P_m^\circ = 0.96$ , the changes in MWD were restricted to an increase in the high molecular weight tail, and no marked increase in LCB was observed. At lower  $P_m/P_m^\circ$ , the changes also comprised an increase in LCB and in the low molecular weight species. In this case a serious decrease in thermal stability was observed (Table 2 and Fig. 14). It is not clear from these measurements to what extent end groups or branch points are responsible for the decrease in thermal stability. However, a comparison with the degradation data for U-polymer prepared with water-soluble initiator at  $P_m/P_m^\circ = 0.96$  (Fig. 15) indicates that the end groups adversely influence the thermal stability. As the resins with the same  $M_n$  but different LCB show similar rates of dehydrochlorination, it could be argued that LCB does not affect the thermal stability to a major extent. The other points in the LCB diagram of Fig. 15 represent resins with variation in both LCB and  $M_n$ .

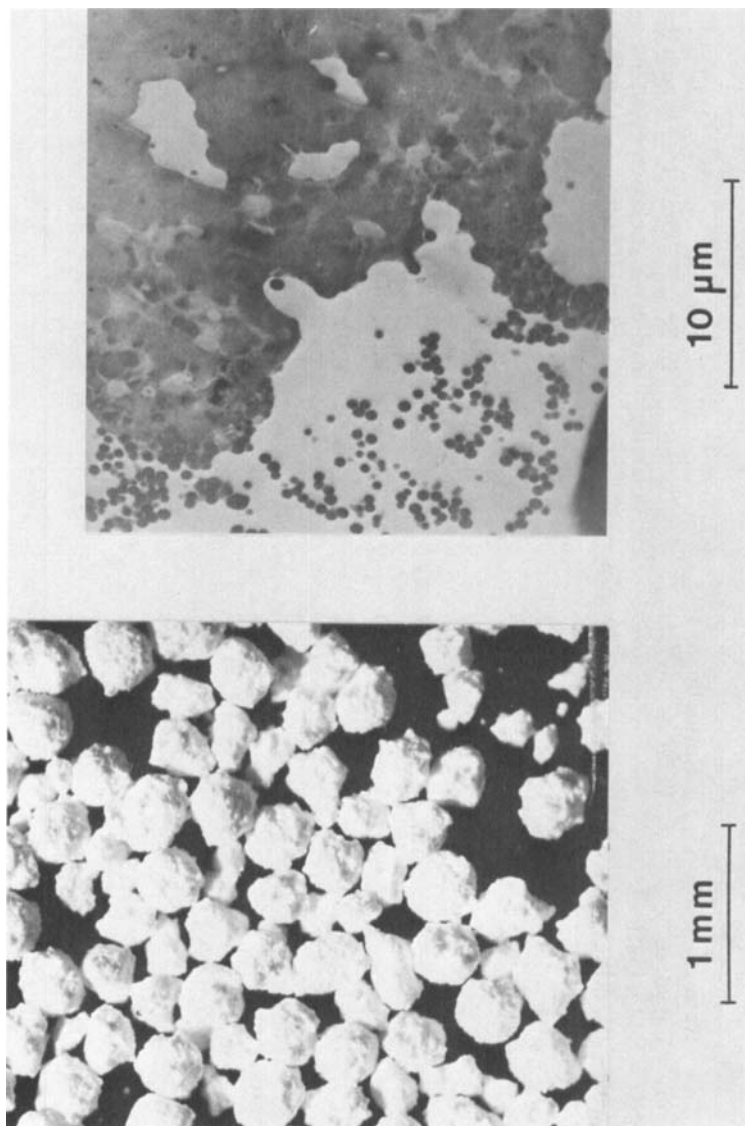


FIG. 13. Morphology of U-polymerizates with mixed water- and monomer-soluble initiators;  $P_m^o/P_m^o = 0.96$ ; 560% conversion.



TABLE 3. Polymerization Series I: Thermal Stability and Processing Properties<sup>a</sup>

No.	Thermal stability										Melt viscosity torque (Nm)
	Conversion (% of seed)	Rate of dehydrochlorination (%/min × 10 <sup>2</sup> )	Reflectance (% after time t)			Porosity (%)	Bulk density (kg/liter)	Time to gelation (min)			
			2 min	10 min	20 min						
S 687	-	1.4	89	87	15	29.1	0.51	0.1			43
1	300	5.6	66	28	20	20.3	0.52	1.6			37
2	680	3.8	69	37	15	11.8	0.58	2.2			40
3	420	3.5	65	32	19	16.7	0.54	2.0			37
4	620	3.1	72	43	20	9.3	0.62	4.3			40
5	390	3.7	67	34	18	16.2	0.54	1.3			38
6	700	5.2	67	35	30	13.4	0.57	1.2			39
7b	300	4.5	68	29	17	22.1	0.49	0.6			36
8b	500	5.7	67	26	14	14.9	0.54	1.2			39
9b	60	4.6	76	46	24	26.4	0.51	0.6			36
10c	80	4.4	76	50	37	22.7	0.53	0.6			37
11	600	1.1	87	70	62	13.6	0.54	5.5			40
12	630	1.3	86	60	17	13.5	0.55	8.7			41

13	530	2.0	d	(46.0) <sup>e</sup>	0.44	0.1	39
14	700	2.2	d	(44.3) <sup>e</sup>	0.41	0.1	36

<sup>a</sup>Initiator: No. 1-10, Liladox suspension; 11-12, Laurox; 13-14, persulfate.

<sup>b</sup> $P_m^o / P_m^o = 0.86$ , all other polymerizations  $P_m^o / P_m^o = 0.96$ .

<sup>c</sup>Increased amount of seed (2 kg instead of 0.5 kg).

<sup>d</sup>Sticks at milling.

<sup>e</sup>Unrealistic value, see text.

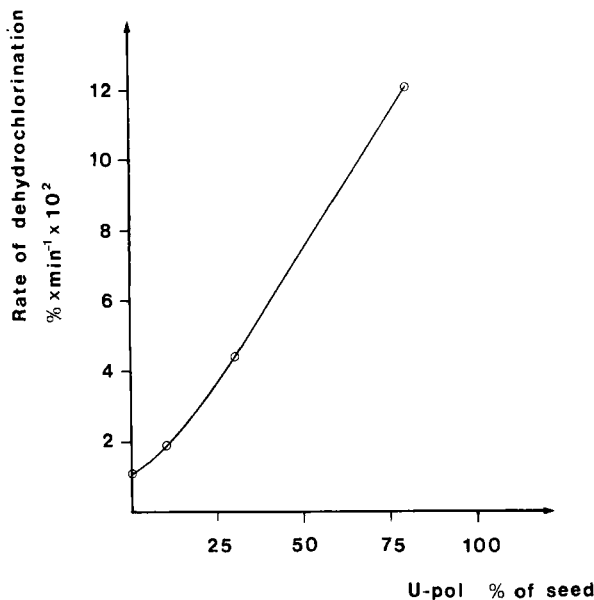


FIG. 14. Changes in thermal dehydrochlorination with conversion:  $P_m/P_m^0 = 0.4$ ; monomer-soluble initiator.

Based on experiments with model compounds [16, 17] and copolymers [18, 19], it was found that branch points with tertiary C-Cl bonds are weak points in the PVC structure. It has been postulated [19] that even one tertiary C-Cl bond per 1000 C could account for the observed rate of dehydrochlorination for ordinary S-PVC. The branch frequency discussed in our experiments is well above 1/1000 C. If the branch points contain tertiary chlorines their effect on the degradation rate should be observed.

No tertiary C-Cl bonds have so far been detected in PVC [20]. This is a consequence of the low LCB, 0.5/1000 C, and the sensitivity limit of the analytical method used, 1/1000 C. By U-polymerization LCB can be increased to such an extent that existing chemical and spectroscopic methods for branch structure investigations could be applied to test if these branch points contain tertiary C-Cl bonds.

### Processing Properties

In Table 3 processing properties are given for some of the polymers investigated. The discoloration tests on film samples gave

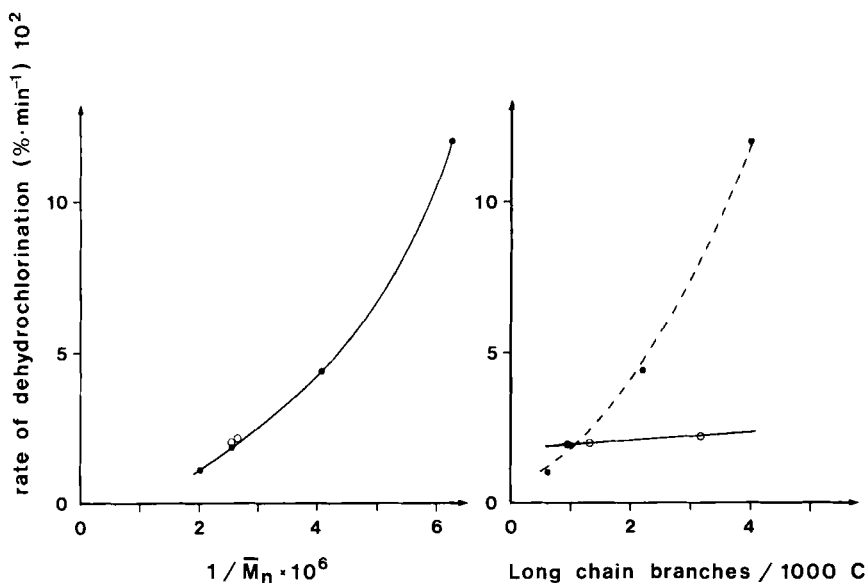


FIG. 15. Influence of end groups and long-chain branch points on thermal dehydrochlorination: (●)  $P_m/P_m^0 = 0.4$ , monomer-soluble initiator; (○)  $P_m/P_m^0 = 0.96$ , water-soluble initiator.

about the same ranking order of the polymers as the dehydrochlorination measurements.

When monomer-soluble initiators were used, the particle size increased and the porosity decreased with conversion. As a consequence, bulk density and time to gelation also increased. Polymerizations with Laurox resulted in products with much longer time to gelation than those with Liladox. The reason for this is not clear. No difference in structure was observed.

As expected from the particle size distributions, U-polymers prepared with water-soluble initiator had very low bulk densities. Due to the aggregated structure, the penetrometer measurements gave no realistic porosity values. As mentioned, microscopic investigations showed that the structure of the seed was retained. The time to gelation was as low as that for the seed.

Judging from Plastograph measurements, all U-polymers tested gave somewhat lower melt viscosity than the seed. In these measurements changes in MWD and LCB should influence the rheology. In

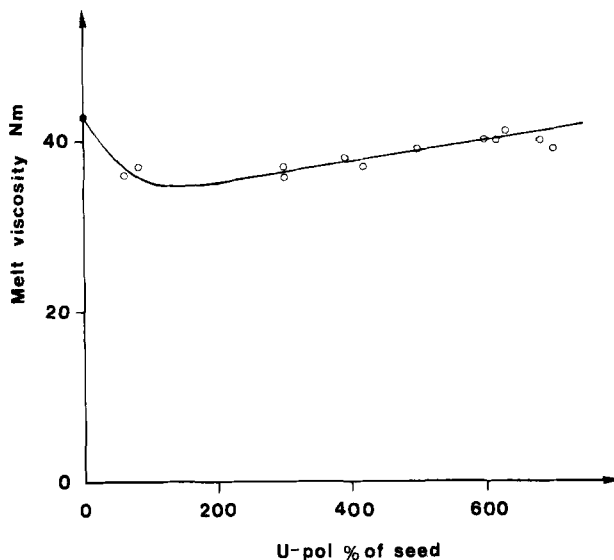


FIG. 16. Changes in melt viscosity with conversion;  $P_m/P_m^0 = 0.96$ , monomer-soluble initiator.

the polymerizates prepared with monomer-soluble initiators, only a minor increase in LCB was noticed.  $\bar{M}_n$  is fairly constant, while  $\bar{M}_w$  and  $\bar{M}_z$  increase with conversion. The changes in melt viscosity are small but show a regular pattern (Fig. 16). The increase in LCB is small but might contribute the initial drop in viscosity. The gradual increase with higher conversions should be due to an increased amount of high molecular weight material.

## CONCLUSIONS

U-polymerization presents a simple means of preparing PVC with a substantial and controlled degree of certain abnormal structures such as long-chain branching and broad MWD. A granular seed substance, e.g., PVC, is necessary in order to obtain a granular polymer and a reasonable polymerization rate. The seed acts as a monomer-absorbing agent and may also be a carrier for the initiator. With an adequate amount of seed no crusts are formed.

Even at pressures close to VCM saturation pressure, changes in the course of the polymerization are noticed. These changes are due to the lack of a liquid monomer phase. With monomer-soluble initiator the polymerization reactions are restricted to the monomer-swollen polymer phase, which result in reduced porosity and auto-acceleration. The increase in molecular weight is supposed to be a result of reduced mobility and thus reduced termination.

At reduced polymerization pressure the mobility in the gel is further reduced. A large reduction in monomer concentration results in low polymerization rate and in the formation of increased amount of low molecular weight material and long-chain branching due to monomer depletion.

With water-soluble initiator polymerization takes place in the water phase at the boundary to the seed polymer, resulting, in new tiny particles loosely aggregated round the seed particles. Even at pressures near saturation, both long-chain branching and broad MWD are obtained without any marked reduction in polymerization rate.

U-polymerization presents features which should be of interest both from a scientific and a technical point of view. Further work on U-polymerization of VCM is in progress.

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