Crosslinked PVC Polymerization: Study on Process Dependencies

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ABSTRACT: A systematic study of how different processes and crosslinking agents affect the crosslinked polymerization of poly(vinyl chloride) (PVC) to be used for plastisol application was carried out. Two processes, microsuspension (MS) and seeded polymerization (SP), and two crosslinking agents, diallyl phthalate (DAP) and 1,3-butanediol dimethacrylate (BDMA), were considered. Variations in degree of polymerization and gel content as functions of conversion, as well as the amount of crosslinking agent, was experimentally investigated for both processes and the results were precisely analyzed. We found that the microsuspension process is much better for crosslinked polymerization of PVC to be used for plastisol application; the seeded polymerization process was restricted by the transfer of crosslinking agents to the polymerization sites. Diallyl phthalate was proven to be a good crosslinking agent as generally known until now. Consequently, to perform crosslinked PVC polymerization in industry, the type of process should be taken into account and proper materials and steps should be set up. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1947–1954, 2002

Key words: crosslinking; PVC; microsuspension; seeded polymerization; DAP

INTRODUCTION

Crosslinking polymer chains is an important way of diversifying the physical and chemical properties of polymers. Generally, mechanical or thermal properties of the crosslinked polymers are enhanced but the processibility is sacrificed. In the case of poly(vinyl chloride) (PVC) resin, crosslinking technology also was investigated as a major tool of enhancing applicability.

PVC is a general purpose plastic material consumed in great quantities around the world today. PVC became a major plastic after World War II, replacing flexible products based on elastomers, leather, and so forth. Later, application of PVC to rigid products such as wood moldings and pipes was introduced with the development of formulating and processing technology. Nowadays, PVC is generally known to have the advantages of low ingredient cost, wide processing versatility, high decorative potential, and so forth, and is used to manufacture various types of products from the highly rigid to the very flexible. Because of the difficulties in handling vinyl chloride monomer (VCM), as well as the low probability of VCM copolymerizing with other monomers, investigations related to PVC mainly focus on the development of formulations with additives and the processing of those formulated compounds, rather than the manufacture or modification of PVC resin.

The need for crosslinked PVC mainly came from PVC plastisol application used in large quantities for floorings, wall coatings, gloves, toys, and others. Plasticized PVC application usually shows relatively poor heat resistance, mechanical resistance, and chemical resistance, whereas it has strong advantages of versatile processing and various shapes and designs. Crosslinking has been known to be the core technology to overcome such disadvantages of plasticized PVC by many investigators until now. Behal and Duchacek[1] classified crosslinking of PVC as follows: (1) degradation crosslinking, (2) photochemical or radiation crosslinking, and (3) chemical crosslinking. However, Roudriguez-Fernandez and Sanchez-Adame[2] modified the classification as two major categories: radiation crosslinking and chemical crosslinking. Whatever the methods were, the study about the crosslinking of PVC mainly focused on crosslinking during processing rather than crosslinking during polymerization for two reasons: the difficulty of polymerizing VCM stated above and the difficulty of processing highly crosslinked PVC resin.

Various methods to crosslink PVC chains during processing were studied by many investigators.[1–7] In their articles, crosslinking of PVC was reported to occur by radiating high-energy beams or by heating for some minutes after the addition of various assistant chemicals such as multifunctional unsaturated monomers, cyclic ethers, dithioltriazine, peroxides, and so on. Most of the assistant chemicals for crosslinking were added during the formulation step for processing, but a few were added during PVC polymerization.

There is also some research about the crosslinked PVC polymerization. Recently, Bao et al. and Luo et al.[8–12] have shown an active investigation about crosslinking of PVC during polymerization reaction and published a series of articles about their results. Those results were invaluable especially in that they set up the detailed theoretical background about the crosslinked PVC polymerization which had remained out of researchers' interest for so long. Before them, Itoh and coworkers[13] published their investigation about crosslinked PVC polymerization in the early 1970s, and their job also gave lots of practically and conceptually precious information to the investigators who were interested in that problem. Itoh and coworkers used diallyl esters and divinyl ethers as crosslinking agents and applied them to two kinds of PVC manufacturing processes, suspension and emulsion. They found that both kinds of crosslinking agents showed different behaviors according to the type of process. In the suspension process, both types of agents were found to act as crosslinking agents, but in the emulsion system, divinyl ethers were shown to have no crosslinking effects.

In this article, we performed a similar study to Itoh and his coworkers', but we took different manufacturing processes into account, microsuspension (MS) and seeded polymerization (SP). Both processes are commercially used to produce PVC resins for plastisol application. We used two kinds of crosslinking agents, diallyl phthalate (DAP) and 1,3-butanediol dimethacrylate (BDMA), and studied process dependency of the crosslinking behavior for those two crosslinking agents. The main purpose of this study is to provide a guide for selecting a proper crosslinking agent and a polymerization process when wanting to control the degree of crosslinking during polymerization of PVC resin for plastisol application.

MANUFACTURING PROCESSES

In this study, two manufacturing processes for PVC were under consideration. One is the microsuspension (MS) process, and the other is the seeded polymerization (SP) process. Both processes are used to produce PVC resins for plastisol application for which ionic emulsifiers are used as the main dispersing agents. The MS process is similar to the usual suspension polymerization process for PVC except that the ionic emulsifying complex system is used instead of the nonionic stabilizing complex system and the homogenizing step is introduced before the main process. Figure 1 shows the schematic of MS process. Initially, each VCM droplet (about 1 μm) acts as a reaction site and contains all the necessary materials, such as monomer, comonomer, initiator, and so on. As the reaction goes on, monomer droplets turn into monomer-swollen PVC particles and finally grow into PVC particles. In the MS process, water acts as the dispersing medium for droplets and particles, and also as the heat-transfer medium.

The situation is much different for the SP process. There is no homogenization step, and so, monomer phase mainly exists as bulk phase or large droplets, as shown in Figure 2. The reaction occurs in the seeds (roughly 0.1–0.6 μm) that are designed to have initiators in it, but all the materials necessary for the reaction, such as mono-
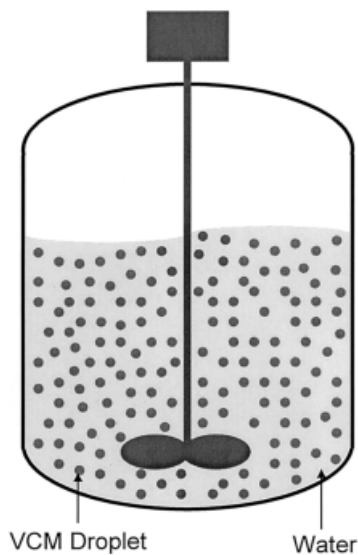
Figure 1 Schematic of microsuspension (MS) process for PVC polymerization.

mer, comonomer, emulsifier, and so on, should be supplied to the reaction sites during the reaction. Therefore, the role of water phase is more important and must act as the route for supply, as well as the dispersing medium and the heat-transfer medium. Further, some physical properties of reactants, such as the solubility and the mass transfer coefficient in water, can influence the polymerization reaction.

EXPERIMENTAL

Crosslinking agents used in the study were DAP and BDMA, and both were not soluble in water (VCM is slightly soluble in water). They are selected after some tests and consideration of practical problems such as cost and availability. The polymerization was carried out in 1-m^3-scale pilot reactor for MS system and 0.3-m^3-scale pilot reactor for the SP system. In the MS system, an oil-soluble initiator and an anionic surfactant complex were used. In the SP system, the redox system was used to activate the oil-soluble initiator contained in the seed; an anionic surfactant complex was also used. The conversion was determined by measuring the weight percentage of the solid parts in the sampled latex during polymerization.

Average degree of polymerization (DP) was measured for PVC dissolved in cyclohexanone by specific viscosity method according to JISK 6721-

1979. Gel content was defined as the ratio of the insoluble part in tetrahydrofuran (THF) to the total PVC resin input and was determined by weighing the separated portion with centrifugation after 24 h of mixing. Also, the amounts of remaining crosslinking agents in the dried samples were measured by gas chromatography (GC) analysis after extracting unreacted crosslinking agents with n-hexane.

RESULTS AND DISCUSSION

First, the relationship between conversion and DP or gel content in both processes is considered. Here, we use only one between DP and gel content for the characterization of the experimental results because we thought DP would not have any meaning at all if the gel were formed. In the case of gel formation, DP is only for the soluble part except for the gel, and thus it cannot stand for the whole system. So, we used only gel content as a variable for y-axis in the graphs, when gel formation was detected.

Figures 3 and 4 contain the results obtained by SP system by using DAP as crosslinking agent. Figure 3 is the comparison of the cases with and without DAP. Without DAP, DP shows a sharp increase to get to the maximum at the initial stage and then keeps the value flatly over 40% conversion. However, when DAP is added by
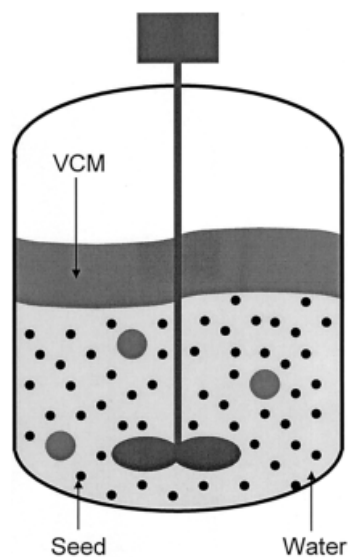

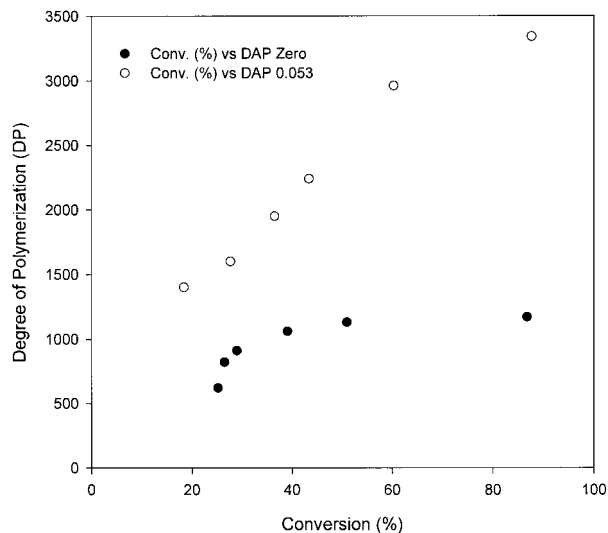**Figure 2** Schematic of seeded polymerization (SP) process for PVC polymerization.

Figure 3 Graph for degree of polymerization (DP) as a function of conversion in the case of the DAP and SP process. The unit of DAP amount is mol % based on initial VCM.
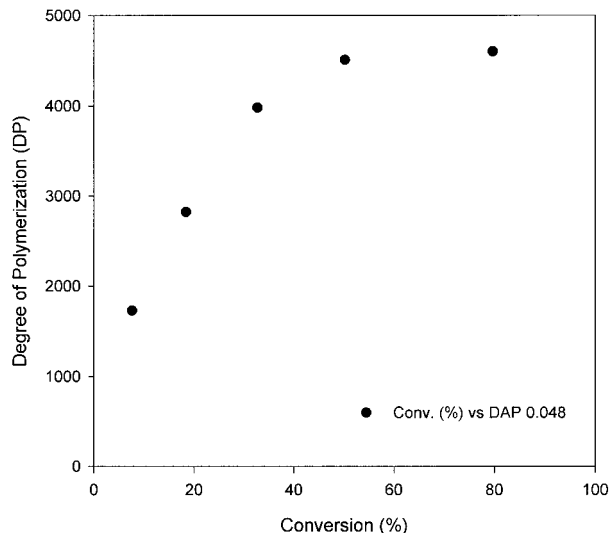

Figure 5 Graph for degree of polymerization (DP) as a function of conversion in the case of DAP and MS process. The unit of DAP amount is mol % based on initial VCM.

0.053 mol % on the basis of initially charged VCM, the DP gradually increases until conversion reaches 90%. In Figure 4, we can find the formation of gel in PVC when DAP is used more than about 0.1 mol %. Here, the gel content gradually increases with the conversion and the amount of DAP used. Those results mean that, in the SP system, crosslinking by DAP occurs constantly until the end of the reaction.

Figures 5 and 6 are the results obtained for the MS process with DAP as the crosslinking agent. The shape of curves and the magnitudes of DP and gel content are shown to be very different from those obtained for the SP process. DP and gel formation show a sharp increase up to about 40% conversion and thereafter almost keep the value constant regardless of the conversion. Further, the extent of crosslinking seems to be
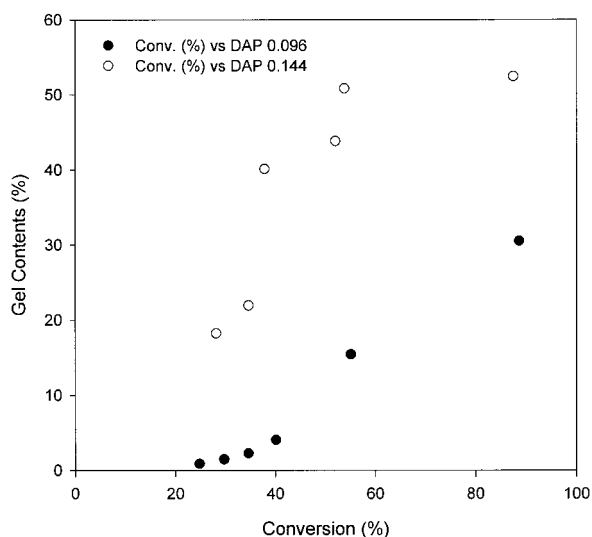

Figure 4 Graph for gel content (%) as a function of conversion in the case of the DAP and SP process. The unit of DAP amount is mol % based on initial VCM.
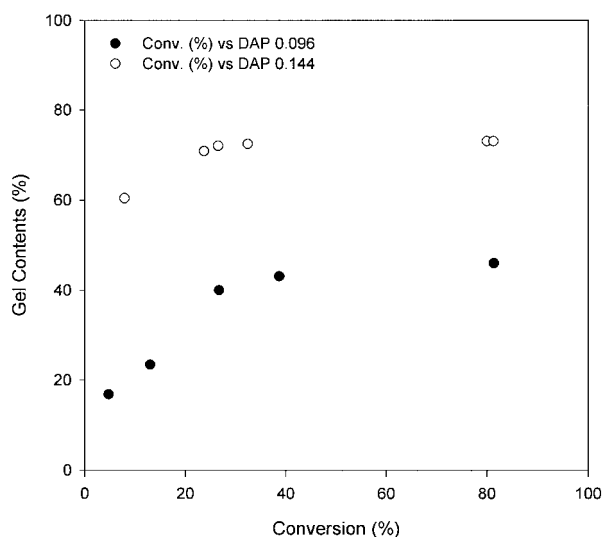

Figure 6 Graph for gel content (%) as a function of conversion in the case of the DAP and MS process. The unit of DAP amount is mol % based on initial VCM.
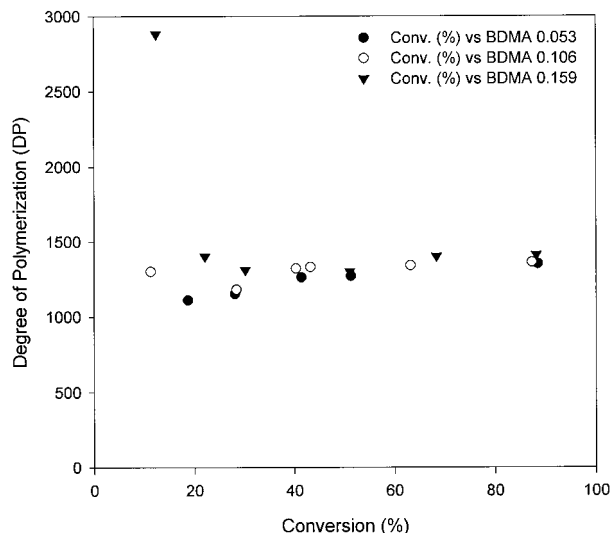
Figure 7 Graph for degree of polymerization (DP) as a function of conversion in the case of the BDMA and SP process. The unit of BDMA amount is mol % based on initial VCM.

greater in the MS system than in the SP system for the same amount of DAP.

The difference mentioned above is thought to be caused by the difference in the transfer mechanism of DAP to the reaction sites between the two processes. In the SP process, DAP is originally dissolved in the bulk VCM phase (see Fig. 2) above water phase composed of water, PVC seeds, and emulsifiers and then is transferred to the reaction sites (i.e., mainly seed) with VCM through water. DAP might be more slowly transferred to the reaction site than VCM because of the much lower solubility in water and the much larger molecular size. Thus, even if the effect of DAP appears at the end of the reaction, the extent of crosslinking is much lower than that of the MS process. However, in the MS process, DAP is dissolved in the VCM droplets which are finely homogenized in water phase before the polymerization begins (see Fig. 1). Each VCM droplet acts as a small reaction domain with all the materials necessary for the reaction from the first and usually leads to a PVC particle without supply of any materials necessary for the reaction from outside. Therefore, almost all the DAP molecules are in the reaction sites from the first, and the consumption of them during the polymerization occurs in the relatively earlier stage of the reaction. Thus in the MS system, the trend of DP or gel content shows a plateau above a certain conversion and the extent of crosslinking is bigger than that for SP process.

Next, the results of crosslinked polymerization with BDMA as the crosslinking agent are shown. Figure 7 shows the relation between conversion and DP in the SP process for 0.053, 0.106, and 0.159 mol % BDMA based on the initially charged VCM. Here, DP remains almost constant regardless of the amount of BDMA after the conversion of about 20%. The DP only at the initial stage of the polymerization is affected by the amount of BDMA, and no gel formation is found irrespective of the amount of BDMA and the conversion. Figure 8 shows the results between conversion and gel content in the MS process for 0.106 and 0.159 mol % BDMA, from which we can see a similar trend with Figure 7. A small amount of gel formation is observed in the MS process because of the difference in the participating mechanism of crosslinking agents in the reaction, as discussed above for DAP. However, conversion-dependent behavior of gel content in the MS process is exactly the same as that of DP in the SP process (Fig. 7), which is different from DAP case where conversion dependencies for the two processes differ (Figs. 5 and 6).

Consequently, the trend of more crosslinking formation in the MS system than in SP is same for both crosslinking agents, DAP and BDMA, but the conversion-dependent behavior is very different for them. BDMA shows a crosslinking reaction only at the very early stage of the polymerization, and that effect disappears quickly as
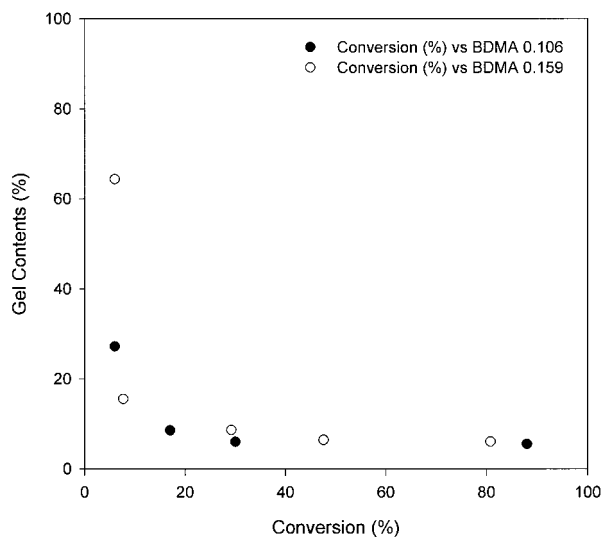

Figure 8 Graph for degree of polymerization (DP) as a function of conversion in the case of the BDMA and MS process. The unit of BDMA amount is mol % based on initial VCM.
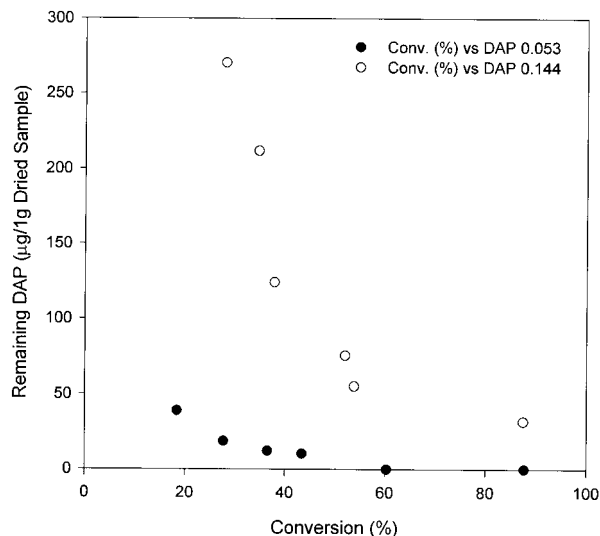
Figure 9 Graph for remaining amount of DAP per 1 g dried sample from polymerization using the SP process as a function of conversion. The unit of DAP amount is mol % based on initial VCM.
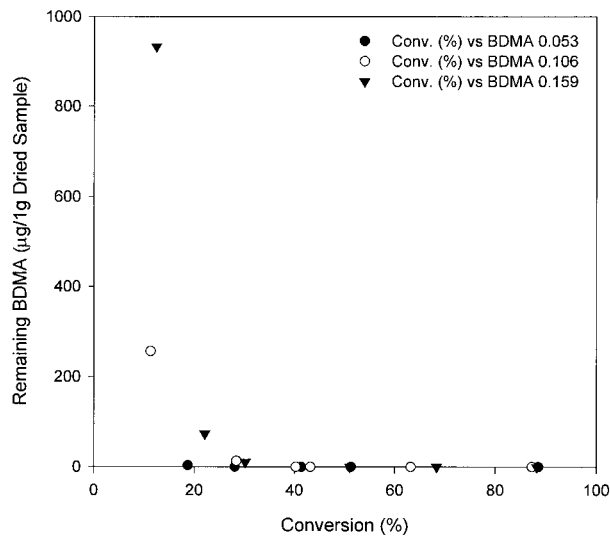

Figure 11 Graph for remaining amount of BDMA per 1 g dried sample from polymerization using the SP process as a function of conversion. The unit of BDMA amount is mol % based on initial VCM.

the polymerization proceeds. As a result, BDMA seems to have no crosslinking effect in PVC polymerization at high conversion, whereas DAP shows good crosslinking ability for PVC polymerization.

To clarify the difference between the two crosslinking agents, the amounts of remaining crosslinking agents in the dried resins from latex

samples during polymerization were examined by using GC analysis as a function of conversion. Figures 9 and 10 show the results between the conversion and the remaining amounts of DAP for both processes. The remaining DAP means DAP which exists in the reaction site and remains unreacted. The remaining amounts of DAP in both processes show similar trends to decrease from
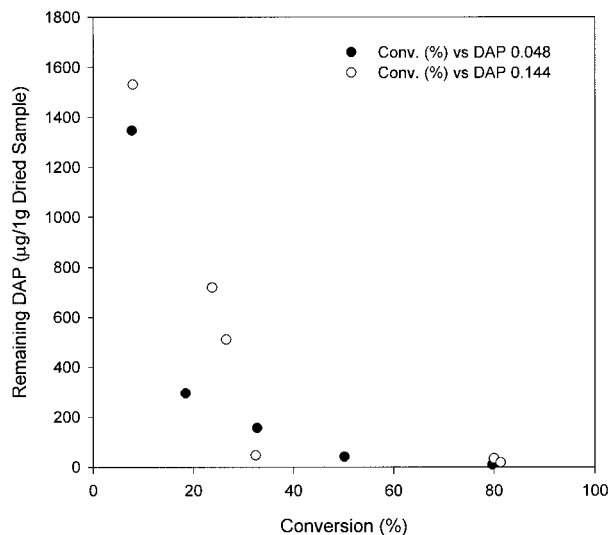

Figure 10 Graph for remaining amount of DAP per 1 g dried sample from polymerization using the MS process as a function of conversion. The unit of DAP amount is mol % based on initial VCM.
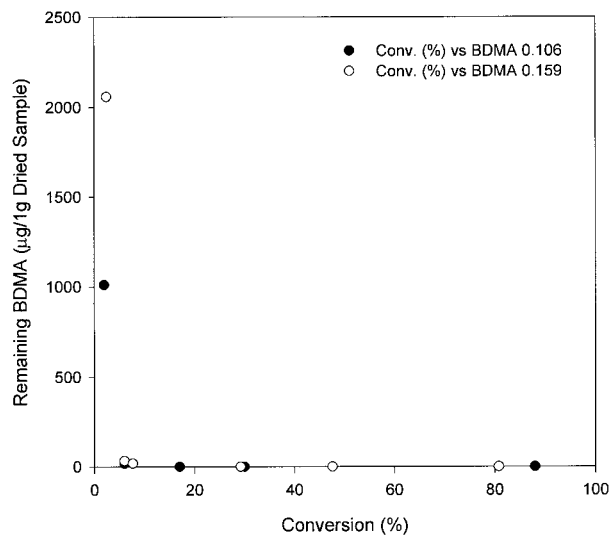

Figure 12 Graph for remaining amount of BDMA per 1 g dried sample from polymerization using the MS process as a function of conversion. The unit of BDMA amount is mol % based on initial VCM.

Table I   Monomer Reactivity Ratios in Radical Copolymerization (cited from Polymer Handbook[14])

Monomer 1	Monomer 2	r_1	r_2	Temp. (°C)
Vinyl chloride (VCM)	Phthalic acid, diallyl ester	1.68	0.38	60
	Methacrylic acid, butyl ester	0.025	30.5	80
		0.05	13.5	45

the beginning until the conversion reaches 90%. The remaining amount increases with the initially charged amount and also is dependent on the process used. In the SP process, the absolute amount of remaining DAP in the latex phase (water + reaction site) is much smaller than that for the MS process for the same amount of initially charged DAP. That finding also supports our opinion about the difference in delivery mechanism of crosslinking agents to the reaction sites between the two manufacturing processes. We also know from Figures 9 and 10 that DAP is detected until the end of the reaction and maybe affects the polymerization to the end.

Figures 11 and 12 show the results of GC analysis of the dried samples polymerized with BDMA for both processes. BDMA appears only below 30% conversion for the SP process and below 10% conversion for the MS process, regardless of the initially charged amount. Almost all BDMA molecules seem to be consumed as soon as they are transferred to the reaction site, much faster than DAP, whereas the dependency on the charged amount and the process shows a similar trend as that of the DAP-remaining amount increases with the amount initially charged and is smaller and longer in the SP process. Here we need to discuss the reason for the difference between DAP and BDMA, comparing DP, gel formation, and remaining amount of crosslinking agent data.

We can find clues for that phenomenon from the reactivity ratios of VCM (M_1) and DAP (M_2) or methacrylate (representing BDMA, M_2) as shown in Table I. Frankly speaking, we could not find any kinetic information about VCM and BDMA and thus decided to use kinetic data for butyl ester methacrylic acid and VCM, even if there might be significant error. However, we thought that it could give conceptually acceptable information. For the VCM and DAP system, r_1 is slightly larger than 1 and r_2 is slightly smaller than 1, but for the VCM and methacrylate system, r_1 is very much smaller than 1 and r_2 is very much larger than 1. From that data, we could

infer that the VCM radical should slightly prefer VCM rather than the allylic group, but very much prefer acrylate than VCM. Further, we can also infer that an allylic radical prefers VCM rather than allylic unit, but an acrylate radical prefers the acrylic unit very much rather than VCM. Consequently, BDMA molecules may produce a long block segment of homopolymer in the early stage of the polymerization by preferentially reacting with themselves and thus may be consumed almost entirely in a very short time so as to show no remaining BDMA and little crosslinking effect.

CONCLUSIONS

From these experimental results, we draw some conclusions. First, the MS process is more appropriate for the effective crosslinking than SP process, because the crosslinking agents can take part in reaction far more easily in the MS process. Second, DAP is more the effective crosslinking agent for PVC polymerization than BDMA, according to the reactivity ratio.

Consequently, we found that the types of processes and crosslinking agents can largely affect the crosslinked PVC polymerization. Therefore, for the modification of PVC resin through crosslinking, type of process and type and amount of crosslinking agent should be properly investigated to achieve satisfactory results.

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