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Influence of Chain Transfer Agent on the Cross-Linking of Poly(*n*-butyl methacrylate-*co*-*N*-methylol acrylamide) Latex Particles and Films

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ABSTRACT: The effects of the concentration of carbon tetrabromide (CBr_4) chain transfer agent on the cross-linking of films formed from a ca. 44 wt % *n*-butyl methacrylate and *N*-methylol acrylamide copolymer latex were studied. The use of CBr_4 greatly decreased the amount of gel in the polymer obtained after the emulsion polymerization process. Gel content measurements in toluene show that there is a limiting value of the gel fraction after thermal curing, which depends on the amount of CBr_4. Calculations using the equations developed by Miller and Macosko show that this is not because of insufficient *N*-methylol acrylamide cross-linking agent in the copolymer. In fact, only ca. 10% of the *N*-methylol acrylamide groups on the polymer chains seem to result in cross-links and contribute to the gel content. This could be due to the constraint on movement limiting the ability to meet and react with the hydroxyl groups on other chains, once the polymer molecule becomes incorporated in the cross-linked network. The thermally cured copolymer film swells to a much lower extent than expected from statistical calculations. This indicates a nonrandom distribution of *N*-methylol acrylamide groups in the polymer particles obtained by the monomer-starved semibatch process, giving a copolymer film with a high degree of cross-linking at the interparticle boundaries and lower values in the interior of the particles.

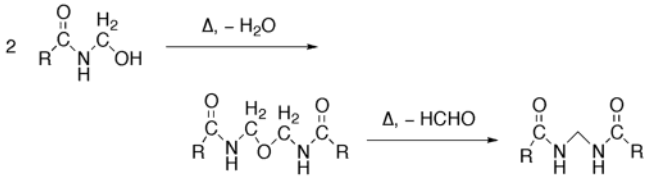
Introduction

Polymers containing *N*-methylol acrylamide (NMA) and prepared by emulsion copolymerization with other vinyl monomers are widely used in applications such as binders for nonwoven fabrics, protective coatings, latex paints, and adhesives. The use of NMA in small amounts (3−7 wt % of the copolymer) results in “self-cross-linkable latexes” which give films with increased tensile strength, impact resistance, abrasion resistance, peel strength, water, detergent, alkali and solvent resistance, dirt pickup resistance, and gloss.[1] The cross-linking mechanism is believed to be the thermal or acid-catalyzed formation of bis(methylene ether) by loss of water and the methylene bridge by the loss of formaldehyde, as shown in Scheme 1,[2] where R represents a polymer chain.

For film formation from latexes, the polymer molecules must be able to diffuse across the interface between the particles to give good interparticle adhesion or welding. It is desirable for the polymer particles to contain linear chains that can diffuse during the film formation process (above the glass transition temperature of the copolymer), and cross-linking occurs after the film is formed. If the latex particles are microgels, that is, they contain cross-linked polymer chains, the resulting film will have poor mechanical properties because of inferior interparticle welding.[3] The presence of cross-links limits the extent of polymer interdiffusion, and the interparticle mixing is restricted to the diffusion of dangling polymer chains anchored to the cross-linked network.[4,5]

In this paper, we describe the results of a study of the cross-linking behavior of high-solids latexes prepared using *n*-butyl methacrylate (BMA) and *N*-methylol acrylamide. The homopolymer of BMA is completely soluble in solvents like toluene and THF. On incorporation of the NMA molecules in the polymer chains, the polymer film obtained after the cross-linking or curing process is expected to be resistant to solvents. Our objective was to develop an emulsion copolymerization recipe that resulted in copolymers that had negligible cross-linking before the curing process and gave high gel contents on thermal curing. The first half of this paper reports experimental results pertaining to the effects of CBr_4 on the molecular weight distribution and cross-linking of the copolymer. The second half deals with statistical calculations based on the method of Miller and Macosko[6,7] that seem to substantiate the experimentally observed trends.

Scheme 1. Cross-Linking Reactions of *N*-Methylol Groups Attached to the Polymer Chains R



Experimental Section

Materials. *n*-Butyl methacrylate (BMA, 99%, CAS # 97-88-1, MW = 142.20 g/mol, Sigma-Aldrich) inhibited by 10 ppm monomethyl ether of hydroquinone (MEHQ, CAS # 150-76-5) was used as the monomer. The monomer was freed from the inhibitor by passing it through an inhibitor-removal column (Sigma-Aldrich). *N*-Methylol acrylamide (NMA, CAS # 924-42-5, MW = 101.11 g/mol, Sigma-Aldrich) was received as a 48 wt % solution in water and was inhibited with 30 ppm of MEHQ. Sodium dodecyl sulfate (SDS, CAS # 151-21-3, MW = 288.38 g/mol, Ultrapure Bioreagent, J.T. Baker) was used as the surfactant, and potassium persulfate (KPS, CAS # 7727-

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Table 1. Recipe for Emulsion Copolymerization of BMA and NMA

seed stage (70 °C, 45 min)		feed stage (70 °C, 150 min)[b]	
ingredient	amount (g)	ingredient	amount (g)
DI water	510.00	DI water	90.0
BMA	60.00	BMA	402.3 (450 cm^3)
SLS	0.735 (5 mM)[a]	NMA	12.0
KPS	0.414 (3 mM)[a]	SLS	3.5
$NaHCO_3$	0.414 (9.7 mM)[a]	CBr_4	2.01, 1.21, 0.81, 0[c]

[a] Concentration in mmol per dm^3 water. [b] Final amount of polymer is ca. 44 wt % of latex. [c] Ca. 0.5, 0.3, 0.2, and 0 wt %, respectively, of the feed stage BMA monomer.

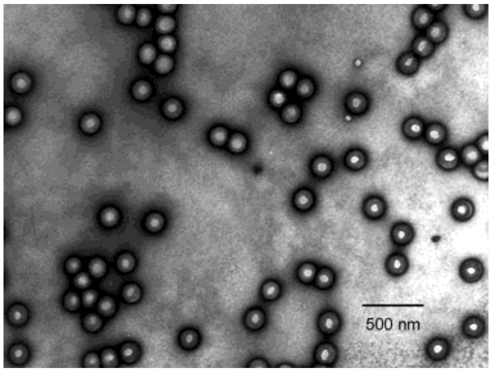

Figure 1. Transmission electron microscope image of polymer particles in the latex prepared using 0.2% CBr_4.

21-1, 99+%, MW = 270.33 g/mol, ACS reagent, Sigma-Aldrich) was used as the initiator. Sodium bicarbonate (CAS # 144-55-8, MW = 84.01 g/mol, Mallinckrodt Baker, Inc.) was used as the buffer. The chain transfer agent CBr_4 (CAS # 558-13-4, 99%, MW = 331.65 g/mol) was obtained from Sigma-Aldrich. Deionized (DI) water was used in the emulsion formulations. The nitrogen gas (Zero Grade 0.5, minimum purity 99.998%, oxygen < 0.5 ppm) was obtained from Airgas. HPLC grade tetrahydrofuran (THF, CAS # 109-99-9, MW = 72.11 g/mol, J.T. Baker) was used as the solvent for gel permeation chromatography. Toluene (CAS #108-88-3, MW = 92.14 g/mol, VWR brand) was used as the solvent for the swelling measurements.

Procedures. Synthesis and Characterization of Latexes. The latexes were prepared in a 2 dm^3 glass reactor using the recipe shown in Table 1. The reactions were carried out at 70 °C under a nitrogen atmosphere. The seed stage consisted of homopolymerization of BMA and was of 45 min duration. The BMA was fed using a LC-5000 precision pump (Isco). The aqueous feed composition of 154/50/7 (parts by weight) DI water/NMA solution/SDS was added using a syringe pump at a rate of 0.690 cm^3/min. CBr_4, when used, was added continuously during the feed stage as a solution in the BMA monomer. From the samples withdrawn at 30 min intervals during the feed stage, the instantaneous conversion of BMA (i.e., the fraction of the total mass of monomer added up to a particular instant during the reaction that has been converted to polymer) was calculated to be greater than 95% after ca. 30 min of the feed stage. Thus, the semibatch polymerization was carried out under monomer-starved conditions and would be expected to produce copolymers of uniform composition. The amount of coagulum on the reactor inserts and in the latex, measured using a sieve with 55 μm pore size, was less than 0.2 wt % based on the total weight of monomer in the recipe. The final latexes were iridescent, indicating that narrow particle size distributions were obtained. The particle diameters in the final latexes determined using capillary hydrodynamic fractionation and dynamic light scattering were ca. 190 nm and did not show any trend with the variation in the amount of CBr_4 added during the feed stage. Figure 1 shows a transmission electron microscope (TEM) image of the latex particles prepared using the recipe in Table 1 and 0.81 g of CBr_4. A few drops of ca. 2 wt % uranyl acetate solution were added to the latex to increase the contrast in the TEM image.

Molecular Weight Distribution. Molecular weight distributions of the polymer samples were measured by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, Water Styragel columns (HR3, HR4, and HR6) at 35 °C, and a Waters 410 differential refractometer detector. The latexes were dried at room temperature, and polymer solutions in THF of ca. 3 mg/cm^3 concentrations were used. THF was used as the eluant at a flow rate of 1 cm^3/min. Narrow molecular weight polystyrene standards ($K = 11.4 \times 10^{-5}$ dL/g, $a = 0.716$) with molecular weights ranging from 580 to 3 800 000 g/mol were used for calibration. The Mark–Houwink constants for poly(BMA) in THF,[8] $K = 14.8 \times 10^{-5}$ dL/g and $a = 0.664$, were used for all the polymer samples.

Determination of Gel Content and Degree of Swelling. The latexes were dried in aluminum pans at room temperature in a fume hood, followed by drying under vacuum to remove the last traces of moisture. Polymer pieces of ca. 3 mm thickness were obtained. The polymer samples were then cured in an oven at an elevated temperature (typically, 150 °C for 30 min). To determine the gel content and swelling, about 1 g of the polymer was immersed in ca. 100 g of toluene for 1 week. The gel was collected by filtering the solution through a 200 mesh stainless steel wire screen. The swollen gel was coherent and usually in a single piece. Weights of the swollen and dry gels were measured. The gel fraction was calculated as the mass of dry gel divided by the original mass of the polymer sample. Gravimetry of the sol gave the amount of polymer that was soluble in toluene. The sol fraction was calculated as the mass of the polymer that was soluble in the solvent divided by the original mass of the polymer sample. The sum of the gel fraction and the sol fraction was close to unity in all the cases, indicating the correctness and reliability of the procedure. The swelling index (SI) was calculated as the mass of the swollen gel divided by the mass of the dry gel.

Results and Discussion

Gel Content and Swelling of Copolymer Films. When the latex prepared in the absence of CBr_4 chain transfer agent was dried at room temperature, the gel content in the uncured film, measured using toluene as the solvent, was 80.4 ± 1.6%. The seed stage homopolymer of BMA was completely soluble in toluene. Since the seed stage polymer constitutes ca. 12.2% of the total polymer in the latex, a maximum gel content of 87.8% is expected. Thus, in the absence of the chain transfer agent, ca. 92% of the feed stage polymer was cross-linked even before the polymer was thermally cured at an elevated temperature. The cross-linking can be physical (e.g., by hydrogen bonding) or chemical. As will be discussed below, the gel content was lower in a polar solvent like tetrahydrofuran, indicating that only a part of the gel insoluble in toluene was chemically cross-linked. Furthermore, the premature cross-linking of the polymer chains could have occurred either during the polymerization or during the film formation process. It was found that the polymer obtained by freeze-drying the latex was also insoluble in toluene, indicating that the cross-linking was not occurring while the latex was being dried at room temperature.

Cross-Linking during Polymerization. To determine the evolution of gel content during the polymerization reaction, the latex samples withdrawn at 30 min interval during the feed stage were frozen to precipitate the polymer. The coagulated polymer was then dried under vacuum at room temperature. The gel contents of these polymer samples were determined using GPC. To obtain the calibration curve, solutions of poly(BMA) in THF with concentrations ranging from 1 to ca. 6 mg

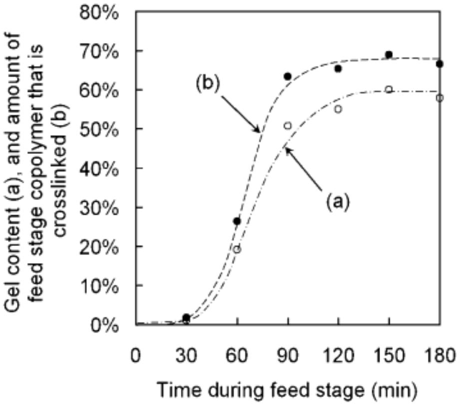

Figure 2. Evolution of gel content during semibatch emulsion copolymerization of BMA and NMA in the absence of CBr_4 (curve a); fraction of the feed stage copolymer that is cross-linked (curve b).

of polymer/g of THF were prepared. These samples were injected into the GPC column, and the area under the detector response vs elution time curve was determined. This area will be proportional to the mass concentration of polymer in the injected sample. Next, the freeze-dried polymer obtained from the latex withdrawn during the feed stage was taken in a glass vial, and THF was added to the vial (ca. 0.06 g of polymer and 10.00 g of THF). The polymer was soaked in the solvent for about a week with regular shaking using a vortex agitator. It was observed that, in the case of samples withdrawn after 60 min of the feed stage, the gel settled at the bottom of the vial on standing. Thus, a significant fraction of the copolymer formed during the feed stage was cross-linked even before the semibatch polymerization was completed. The evolution of gel content was quantified by injecting the clear supernatant solutions in the vials into the GPC column, determining the area under the detector (refractive index) response vs elution time curves and, hence, the concentration of the polymer in the sol, using the calibration. Knowing the total concentration of the polymer (gel + soluble) from the sample preparation step and the concentration of the polymer in the sol from GPC measurements, the fraction of the polymer that was not cross-linked could be obtained. The gel fraction is simply one minus the sol fraction. Figure 2 shows the evolution of gel content during the reaction, and the fraction of the polymer formed during the feed stage that is cross-linked (accounting for the seed stage PBMA which is not cross-linked). It is clear that cross-linking begins to occur after ca. 30 min of the feed stage, and after ca. 90 min, 60−70% of the polymer formed during the feed stage is already cross-linked.

Volfova et al. also made a similar observation in their experiments of semibatch emulsion copolymerization of NMA with styrene and *n*-butyl acrylate.[9] They measured the evolution of gel content during the feed stage of a semibatch emulsion polymerization process and found that the polymer formed even during the early stages of the feed stage had a relatively high amount of gel. The gel content increased until the end of the reaction. They concluded that the cross-linking reaction between the methylol groups occurred during the polymerization. They attributed this to the following two effects. The highly acidic reaction medium (pH 2−3) and the presence of the peroxy disulfate initiator catalyzed the reaction in Scheme 1 at the low reaction temperature of 40 °C. Also, they proposed that the strongly acidic surface sulfate groups derived from the initiator resulted in the hydrolysis of the ester bonds in butyl acrylate during the polymerization, and the NMA reacted with the resulting carboxylic acid group.

Table 2. Effect of Amount of CBr_4 on the Gel Content and Swelling of Films (in Toluene) Formed at Room Temperature, before and after Thermal Curing

CBr_4 (%)[a]	curing of film formed at rt	gel content (%)[b]	swelling index[b]
0	uncured	80.4 (1.6)	11.0 (0.2)
0	150 °C, 30 min	88.3 (0.7)	12.1 (0.4)
0.5	uncured	10.9 (0.0)	22.6 (0.4)
0.5	150 °C, 30 min	35.3 (1.0)	17.5 (0.7)

[a] In wt % based on feed stage BMA. [b] The values in the parentheses are the standard deviations.

The pH of our system buffered with $NaHCO_3$ was between 6.5 and 7 throughout the reaction. For the methylene bridge formation (Scheme 1) to occur under these pH conditions and over the time scale of the polymerization reaction, temperatures greater than the reaction temperature of 70 °C will be required. The premature cross-linking occurred even when there was no $K_2S_2O_8$ to catalyze the methylene bridge formation. In a separate experiment, 0.74 g of a water-soluble azo initiator, 4,4′-azobis(cyanopentanoic acid) (Vazo 68, DuPont), was used with an equal mass of $NaHCO_3$ in the recipe in Table 1 instead of $K_2S_2O_8$. The pH of the emulsion was almost neutral. In this case also, the film formed at room temperature consisted of ca. 88 % of polymer that was insoluble in toluene even before thermal curing. Thus, the cross-linking was not solely because of methylene bridge formation during the polymerization reaction.

We propose the following mechanism for the premature cross-linking. The NMA unit that is incorporated in the polymer chain has a labile α-hydrogen atom on the polymer backbone. Because of the high concentration of polymer in the polymer particles during the monomer-starved semibatch emulsion polymerization, a free radical can undergo chain transfer to polymer by abstraction of the α hydrogen atom of NMA. This process results in branching of the polymer chain. Cross-linking occurs when two branch ends meet and terminate each other. An evidence for the proposed mechanism is the fact that strong oxidants like $K_2S_2O_8$, H_2O_2, etc., attack the polyacrylamide or N-substituted polyacrylamide backbone and gel polyacrylamide solutions containing high molecular weight polymer.[10] Also, Kamogawa and Sekiya suggest “an undetermined hydrogen-liberating reaction with a radical mechanism” for the cross-linking of NMA containing polymers.[11] Use of a chain transfer agent is expected to minimize the branching steps and, therefore, avoid premature cross-linking. The following experimental results show that, by varying the concentration of CBr_4 chain transfer agent in the BMA feed, one can control the gel content in the polymer films before and also after thermal curing.

When 0.5% CBr_4 was used in the recipe of Table 1, the gel content in the uncured polymer measured using toluene dropped from 80.4 ± 1.6% (in the absence of CBr_4) to 10.9 ± 0.05%. However, even after curing at 150 °C for 30 min, the gel content did not increase beyond 35.3 ± 1.0%. Moreover, the gel content did not increase with additional time beyond 30 min. Table 2 summarizes the results of the swelling experiments for polymers prepared without CBr_4 and in the presence of 0.5% CBr_4. The numbers in the parentheses are the

Table 3. Effect of Amount of CBr_4 on the Gel Content and Swelling of Films (in Toluene) Cured at 150 °C for 30 min

CBr_4 (%)[a]	gel content (%)	swelling index
0.5	35.3 (1.0)	17.5 (0.7)
0.3	58.6 (2.5)	13.5 (0.2)
0.2	71.1 (1.4)	11.0 (0.1)
0	88.3 (0.7)	12.1 (0.4)

[a] In wt % based on feed stage BMA.

Table 4. Influence of Solvent on the Determination of Gel Content and Swelling

CBr_4 (%)[a]	solvent	gel content (%)	swelling index
0	toluene	80.4 (1.6)	11.0 (0.2)
0	THF	57.4 (1.8)	20.9 (2.7)
0.2	toluene	19.6 (0.4)	27.3 (1.3)
0.2	THF	3.4 (1.2)	37.8 (12.7)

[a] In wt % based on feed stage BMA.

standard deviations of the measurements from the mean values. The latexes were ca. 1 month old, were dried at room temperature, and swollen in toluene. When 0.2% CBr_4 was used, the gel content of the uncured polymer measured in toluene was 19.6 ± 0.4%. Table 3 gives the gel content and swelling index of copolymer films cured at 150 °C for 30 min as a function of the amount of CBr_4 used in the feed stage recipe. Thus, the use of CBr_4 decreases the premature cross-linking of polymer chains. The gel content in the thermally cured copolymer film depends on the amount of CBr_4 used during the synthesis. The gel content is lower and the degree of swelling is greater at higher concentrations of CBr_4.

Effect of Solvent on Gel Content Values. Yeliseeva found that intermolecular hydrogen bonds (H-bonds) at the particle interface gave polymer films with higher strength and elastic modulus and lower water absorption compared to the films cast from solution.[12] She proposed that the degree of interaction due to hydrogen bonds of oriented methylol acrylamide groups in the latex film was greater compared to the randomly located methylol acrylamide groups in the solvent cast film. The NMA mers in the copolymer chains are both H-bond donors and H-bond acceptors because of the −OH and −NH groups. The BMA mers containing oxygen atoms are H-bond acceptors. Hydrogen bonding between the donor and acceptor groups on two different polymer chains can also result in cross-linking besides the covalent cross-links. However, a polar solvent like tetrahydrofuran is expected to break the H-bonds giving a lower fraction of gel. Table 4 compares the gel content and swelling of the films in toluene and tetrahydrofuran. The films were cast at room temperature from latexes prepared using 0 and 0.2% CBr_4 during the feed stage. The indication is that substantial hydrogen bonding is present in our polymer films.

Molecular Weight Distribution in Uncured Copolymer. Figure 3 shows the molecular weight distributions of the polymer in the final latexes prepared using the recipe in Table 1 with varying amounts of CBr_4. The polymers obtained by drying the latexes at room temperature were almost completely soluble in THF. In Figure 3, dw/d log M obtained by GPC is plotted against log M, where $w(M)$ is the weight fraction of polymer chains in the sample with molecular weights less than M.[13]

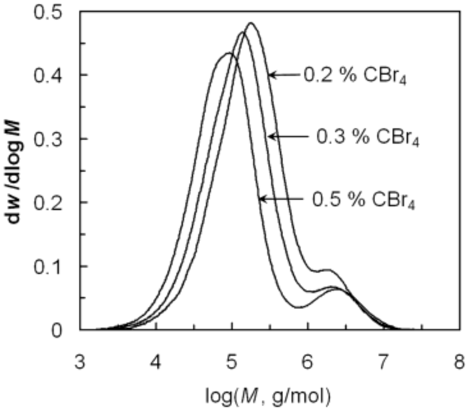

Figure 3. Effect of concentration of CBr_4 on the molecular weight distributions in polymers prepared using the recipe in Table 1.

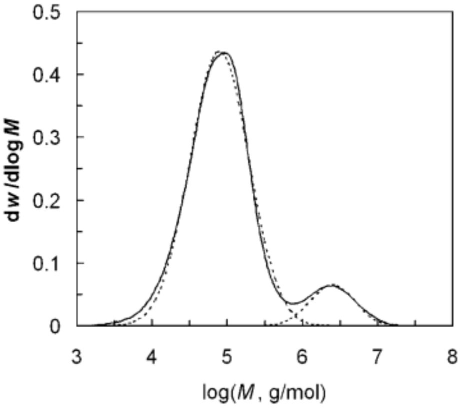

Figure 4. Experimental MWD (solid curve) and empirical fit assuming Gaussian peaks (dashed curves) for the polymer prepared using 0.5% CBr_4.

Table 5. Influence of the Amount of CBr_4 in the Feed Stage, on the Molecular Weight Distribution of the Feed Stage Polymer

CBr_4 (%)[a]	$[CBr_4]$/ $[BMA]$[b]	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	PDI = $\bar{M}_w/\bar{M}_n$	x_n
0.5	0.002 13	52 098	118 188	2.27	366
0.3	0.001 28	76 030	190 641	2.51	535
0.2	0.000 85	104 628	271 740	2.60	736

[a] In wt % based on feed stage BMA. [b] Molar ratio of CBr_4 to BMA in the feed.

The molecular weight distributions show two distinct peaks. The high molecular weight peaks correspond to the seed stage BMA homopolymers that were formed in the absence of any chain transfer agent. The peaks at the lower molecular weights correspond to the feed stage polymer and shift to lower molecular weights with increasing amounts of CBr_4. It was found that deconvolution assuming a normal (Gaussian) distribution[14] gave a good fit for the dw/d log M vs log M data, from which the number-average molecular weight $\bar{M}_n$ (g/mol) and weight-average molecular weight $\bar{M}_w$ (g/mol) of the feed stage copolymer were calculated.[13]

Figure 4 compares the dw/d log M obtained from the GPC detector response, and the empirical fit assuming Gaussian peaks, for the polymer sample prepared using 0.5% CBr_4. The fit is quite satisfactory. Table 5 gives $\bar{M}_n$, $\bar{M}_w$, and the number-average degree of polymerization, x_n, for the feed stage polymer (lower molecular weight peak). The data show the narrowing of MWD with increasing amounts of chain transfer agent. x_n was estimated by dividing $\bar{M}_n$ by the molecular weight of BMA (142.2 g/mol). As expected, the number-average

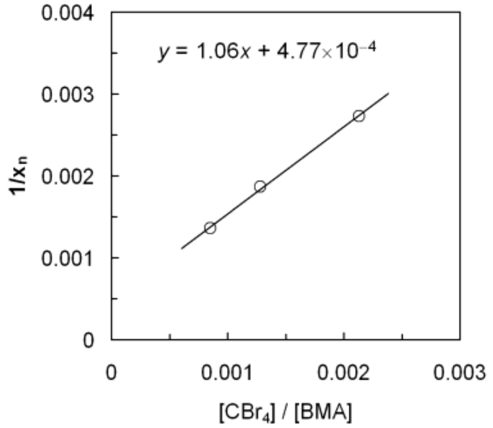

Figure 5. Plot of the reciprocal of the degree of polymerization in the final polymer vs the molar ratio of CBr_4 and BMA during the feed stage.

degree of polymerization decreases with increasing concentration of CBr_4.

In Figure 5, $1/x_n$ is plotted against the molar ratio of CBr_4 to BMA in the feed. The plot is linear with a slope of 1.06. This value gives the chain transfer constant of CBr_4 to BMA at 70 °C and seems to be consistent with the value expected by Geurts et al.[15] The molecular weight distribution of the feed stage polymer remains almost unchanged throughout the feed stage.[13] Hence, it is reasonable to assume that the MWD of the polymer in the final latex represents the instantaneous distributions during the feed stage.

Calculation of Postgel Properties Based on Miller and Macosko's Approach. The un-cross-linked polymer sample can be visualized as consisting of linear polymer chains with hydroxyl pendant groups (from the NMA units). The number of hydroxyl groups per polymer chain is called the functionality, f, of the polymer molecule. Because the feed stage polymer has a broad molecular weight distribution, the polymer chains will have different functionalities depending on the number of NMA molecules copolymerized with the BMA molecules in each chain. The cross-linking reaction can be considered as the stepwise reaction of, in Miller and Macosko's notation, A_{f_i}'s, the polymer chains with, f_i functional groups (−OH groups). Bauer and Dickie[16] have found that the effective cross-link density during the curing of water-based and solvent-based acrylic resins cross-linked with melamines calculated by this method correlated well with the solvent resistance of the films.

Consider a polymer chain with functional group A. $P(F_A^{out})$ is the probability that another chain anchored to the polymer at A has a finite molecular weight. In other words, F_A^{out} is the event that the chain looking *out* of the molecule through the functional group A is finite and is not attached to an infinite network (gel). Using conditional probabilities, an expression for $P(F_A^{out})$ is

$$P(F_A^{out}) = P(F_A^{out}|\text{A reacts})\, P(\text{A reacts}) + P(F_A^{out}|\text{A does not react})\, P(\text{A does not react}) \tag{1}$$

Let p denote the extent of reaction of the functional group A, i.e., the fraction of the total −OH groups that have undergone the condensation reaction. The probability that a functional group selected at random has reacted, P(A reacts), is the extent of reaction, p. Conversely, the probability that the functional group A has not reacted, P(A does not react), is $(1 - p)$. $P(F_A^{out}|\text{A does not react})$ is the conditional probability that the chain attached to A is not of an infinite molecular weight, given that A has not reacted. This is unity, since an unreacted functional group on a polymer chain cannot attach that chain to the gel. Similarly, $P(F_A^{out}|\text{A reacts})$ is the probability of the functional group leading to an infinite network upon reaction. Following the recursive procedure of Miller and Macosko, $P(F_A^{out})$ can be related to p by eq 2.

$$p\sum_i a_{f_i} P(F_A^{out})^{f_i-1} - P(F_A^{out}) - p + 1 = 0 \tag{2}$$

where a_{f_i} is the mole fraction of the A groups that belong to the A_{f_i} polymer chains.

$$a_{f_i} = \frac{f_i A_{f_i}}{\sum_i f_i A_{f_i}} \tag{3}$$

In eq 3, A_{f_i} denotes the moles of polymer chains with functionality f_i. Since in a monomer-starved process all the polymer chains have the same overall composition, the molecular weight of the polymer chain, $M_{A_{fi}}$ (g/mol), is proportional to the functionality f_i. Thus

$$M_{A_{fi}} = Kf_i \tag{4}$$

The substitution $f_i = M_{A_{fi}}/K$ into eq 3 gives

$$a_{f_i} = \frac{M_{A_{fi}} A_{f_i}}{\sum_i M_{A_{fi}} A_{f_i}} \tag{5}$$

Therefore, a_{f_i} is simply the weight fraction of the polymer molecules with molecular weight $M_{A_{fi}}$ or the weight distribution of molecular weights. The weight distribution, $W(M)$, is the derivative of cumulative distribution function, $w(M)$, with respect to the molecular weight, M, and can be obtained from dw/d log M.

Sol Content. An A_{f_i} molecule will be a part of the sol if all f_i of its functional groups are attached (or, lead out) to finite chains. Hence, w_s, the weight fraction of soluble material in the network at a given extent of reaction, is given by

$$w_s = \sum_i w_{A_{fi}} P(F_A^{out})^{f_i} \tag{6}$$

where $w_{A_{fi}}$ is the weight fraction of A_{f_i} in the mixture.

Cross-Link Density. Following the reasoning of Miller and Mocosko, for a polymer chain A_{f_i} to be an effective part of the network, at least three of its functional groups must lead out to the infinite network. If only one functional group reacts, the polymer chain will be just dangling on the network (cf. chain 3 in Figure 6); if two groups react, A_{f_i} will be a part of the chain connecting two effective junction points but is not an effective junction point (cf. chain 4 in Figure 6).

The probability that an A_{f_i} molecule is an effective cross-link of degree m is

$$P(X_{m,f_i}) = C(f_i,m)\, P(F_A^{out})^{f_i-m}[1 - P(F_A^{out})]^m \tag{7}$$

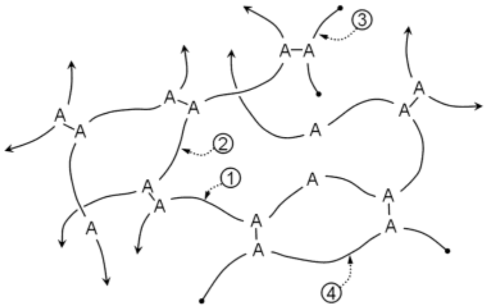

Figure 6. Schematic of cross-linking of polymer chains in the copolymer film. A represents the NMA units in the chains. Chains 1 and 2 have effective junction points. Chains 3 and 4, with one and two reacted functional groups, respectively, just dangle on to the network and do not contribute to the concentration of effective junction points.

where $C(f_i,m)$ is the binomial coefficient. In other words, $P(X_{m,f_i})$ is the probability that exactly m out of the f_i hydroxyl groups of the A_{f_i} polymer chain are effective junction points. Thus, the concentration of the effective cross-links of degree m is given by

$$[X_m] = \sum_{f_i=m}^{f_k} [A_{f_i}]_0 P(X_{m,f_i}) \tag{8}$$

where $[A_{f_i}]_0$ is the initial concentration of A_{f_i} molecules and f_k is the highest functionality. The total cross-link density, X (mol/cm^3), is the sum of $[X_m]$'s from $x = 3$ to f_k. $[A_{f_i}]_0$ is calculated using eq 12.

$$[A_{f_i}]_0 = \frac{\rho w_{A_{fi}}}{M_{A_{fi}}} \tag{9}$$

where ρ (g/cm^3) is the density of the polymer.

Analysis of Experimental Data. NMA is a water-soluble monomer, and its homopolymer is also water-soluble. During the feed stage, a part of the added NMA monomer is incorporated in the polymer particles by copolymerization with BMA, while the remaining polymerizes in the aqueous phase to form water-soluble polymer. It is mainly the fraction of NMA incorporated in the particles that will result in the cross-linking of the polymer chains. Ultracentrifugation was used to separate the aqueous phase of the latex (serum) from the polymer particles. For the case of 0.2% CBr_4, the total mass of solids in the serum was determined by ultracentrifugation to be ca. 6.38 g. This will comprise the water-soluble polymer, the initiator, the buffer, and a fraction of the total amount of surfactant that is in equilibrium with the molecules adsorbed on the polymer particles. ^{1}H NMR spectroscopy of the serum-phase solids showed that the water-soluble polymer was mainly a homopolymer of NMA. Quantitative analysis gave the mass of NMA incorporated in the polymer particles equal to ca. 6.79 g.[13] Thus, ca. 57% of the NMA used in the recipe was incorporated in the polymer particles, and the rest remained in the aqueous phase mainly as water-soluble polymer and, to a small extent, as unreacted monomer. The total mass of water-soluble solids in the serum did not show a significant variation with the amount of chain transfer agent used in the recipe with an average value of 6.42 ± 0.35 g. Because the monomers were fed at a rate slow enough that each added increment reacted almost completely before the next increment was introduced, each copolymer chain is expected to contain BMA and NMA in the mass ratio of ca. 402:7 (same as the overall composition at the end of the reaction).

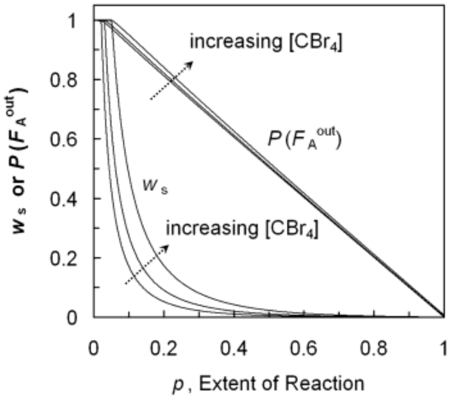

Figure 7. Effect of CBr_4 concentration (0.2, 0.3, and 0.5 wt % based on feed stage BMA) on w_s and $P(F_A^{out})$.

Thus, $w_{A_{fi}}$, the weight fraction of molecules with functionality f_i, could be calculated using the weight distribution of molecular weights. Figure 7 shows the expected evolution of w_s and $P(F_A^{out})$ calculated using eqs 2−6 for 0.2, 0.3, and 0.5 wt % CBr_4 in the feed stage. For a given extent of reaction, p, beyond the gel point, the weight fraction of sol is higher when the CBr_4 concentration is higher. This is in accord with the experimental results and is expected because, while the number of polymer chains to be cross-linked increases with an increase in CBr_4, the total number of −OH groups that can undergo the cross-linking reaction remains the same. The weight fraction of sol, w_s, is unity up to the gel point. Beyond the gel point, a network of infinite molecular weight is formed, and w_s starts decreasing rapidly as p increases. The extent of reaction at the gel point is seen to be quite low (ca. 2% in the case of 0.2% CBr_4) and increases with an increase in the amount of CBr_4.

Table 3 gives the experimentally determined gel fractions, the remainder being the sol. From the recipe in Table 1, it is seen that ca. 12.7 wt % of the total polymer is the seed stage BMA homopolymer that is not cross-linked. Therefore, the fraction of the feed stage copolymer that dissolved in the solvent, w_s, can be calculated by subtracting 12.7% from the experimentally measured sol fraction. The extent of reaction, p, for a given w_s and CBr_4 concentration can be read from Figure 7 and so also $P(F_A^{out})$ corresponding to this p. Using $P(F_A^{out})$ and eqs 7−9, the effective cross-link density can be estimated. The results are shown in Table 6. f_{avg} is the average functionality of the polymer chains calculated from the number-average molecular weight, $\bar{M}_n$, given in Table 5. n (mol/cm^3) is the concentration of active network chain segments obtained using the Flory−Huggins equation for swelling of a cross-linked polymer (eq 10):[17]

$$-[\ln(1 - v_2) + v_2 + \chi_1 v_2^{\,2}] = V_1 n\left[v_2^{\,1/3} - \frac{v_2}{2}\right] \tag{10}$$

where v_2 is the volume fraction of polymer in the swollen gel, V_1 (cm^3/mol) is the molar volume of the solvent, χ_1 is the Flory−Huggins polymer−solvent interaction parameter, and n (mol/cm^3) is the concentration of active network chain segments. The values of n were deter-

Table 6. Calculated Extents of Reaction and Effective Cross-Link Densities in the Thermally Cured Polymer

CBr_4 (wt %)	w_s	f_{avg}	p	$P(F_A^{out})$	X ($\times 10^5$) (mol/cm^3)	ν_c ($\times 10^5$) (mol/cm^3)	n ($\times 10^5$)[a] (mol/cm^3)
0.5	0.55	8.3	0.0976	0.9584	0.0337	0.0256	2.224
0.3	0.29	12.7	0.0992	0.9317	0.125	0.132	3.638
0.2	0.14	16.5	0.1248	0.8947	0.227	0.329	5.143

[a] Calculated from swelling index in toluene.

mined using the data for swelling index in Table 3, polymer and solvent densities of 1.055 and 0.8577 g/cm^3, respectively, and an interaction parameter for poly(*n*-butyl methacrylate) and toluene equal to 0.1508 at 25 °C.[18] The copolymer contains ca. 97.6 mol % of BMA. Hence, an interaction parameter same as that for poly(*n*-butyl methacrylate) was used.

The low extents of reaction of the −OH groups can be rationalized on the basis of the decreased freedom of movement of the polymer chains upon cross-linking. The probability that the −OH groups on two polymer chains that are cross-linked meet and react will be low. In the case of self-cross-linking of polymer chains, one would expect the concentration of effective cross-links, X, and the concentration of active network chain segments, n, to be approximately the same. However, the values of X in Table 6 are at least an order of magnitude lower than n. The cross-linked gel swells to a much smaller extent than theoretically predicted.

Possible explanations for the discrepancy in the observed and predicted values of cross-link densities are the following. First, physical cross-links due to trapped entanglements contribute to the cross-link density. The critical entanglement molecular weight of poly(*n*-butyl methacrylate), M_e, the molecular weight above which the polymer chains in the melt are entangled, can be estimated using $M_e \approx 30C_\infty M_0$, where C_∞ is the characteristic ratio and M_0 is the monomer molecular weight,[19] which for poly(*n*-butyl methacrylate) are 8.50[20] and 142.2 g/mol, respectively. Thus, the polymer chains in our copolymer samples, with a number-average molecular weight that exceeds that exceeds the critical entanglement molecular weight of ca. 36 000 g/mol, will therefore be entangled.[21] These entanglements are made permanent upon cross-linking and contribute to the elastic resistance to the expansion of the network structure by the solvent. Physical cross-links due to entanglements have not been accounted for in the calculation of X.

Second, the monomer-starved semibatch process and the hydrophilicity of NMA result in a radial concentration gradient of NMA units in the polymer particles. A core−shell morphology of the polymer particles is expected, with the NMA units present mainly in the 45 nm thick copolymer shell surrounding the 100 nm diameter core (the PBMA seed particle). Transmission electron microscopy and atomic force microscopy of the copolymer particles and thermally cured films, respectively, from a latex prepared using a similar recipe, confirm the core−shell morphology.[13] There is a nonuniform distribution of cross-linkable NMA units across the cross section of the polymer particle with the NMA units present mainly in the shell. Hence, during the thermal curing of the film, the cross-linking occurs mainly in the shell, and the core polymer is not cross-linked. The cross-linking in the thermally cured film is not uniform, and the polymer network is not homogeneous, as assumed in both the Miller−Mocosko and the Flory−Huggins theories. The swelling of the heterogeneous gel, with a higher concentration of cross-links in the interconnected particle shells (which constitute the matrix in the thermally cured film) and no cross-links in the particle cores (which become “soft” inclusions of un-cross-linked polymer within the cross-linked matrix), will be lower compared to the swelling of a homogeneous gel with the same overall number of cross-link points per unit volume of the polymer but a uniform distribution of the cross-link points.[22]

Magnet et al.[23] have studied the mechanical properties of films cast from styrene−butyl acrylate latexes functionalized with glycidyl methacrylate (GMA). The cross-linking reaction was between the epoxy groups of GMA and an external cross-linking agent hexamethylenediamine. The functionalized copolymers were prepared by batch and semibatch processes. The radial distribution of the GMA units was determined by titration of the epoxy groups of GMA. They concluded that during the batch process the highly reactive GMA monomer was fully consumed early in the reaction. The epoxy groups were therefore buried inside the polymer particles. However, the semibatch process resulted in uniform radial distribution of GMA across the particle, while a semibatch process with delayed GMA addition gave a latex with most of the GMA units located near the surface of the particles. On the basis of the mechanical properties of the cross-linked films, they proposed that when most of the GMA groups were present near the surface of the latex particles, the film consisted of a cross-linked honeycomb network running through the soft, weakly cross-linked matrix. However, when the epoxy groups were uniformly distributed within the latex particles, the film consisted of a cross-linked matrix with soft inclusions.

Third, eqs 7 and 8 are derived assuming that all groups react independent of one another. In reality, when a few −OH groups on a polymer chain react and attach the chain to the gel, the reactivity of all the other groups on the chain becomes low due to steric restrictions. Fourth, we have assumed that no intramolecular reactions occur. However, two −OH groups on a long chain can react, and this could be another source of deviation from theoretical predictions.

Conclusions

The problem of premature gelation in NMA based latexes prepared by monomer-starved semibatch emulsion polymerization, possibly due to the hydrogen abstraction mechanism, can be overcome by the use of a chain transfer agent. However, the amount of chain transfer agent influences the cross-linking and swelling of the thermally cured copolymer film. In the absence of any chain transfer agent, the copolymer formed during the feed stage is almost completely cross-linked even before the thermal curing process. When CBr_4 chain transfer agent is used in the range of 0.2−0.5 wt % of feed stage BMA, the uncured copolymer film is almost completely soluble in a solvent. The amount of gel formed at the end of the thermal cross-linking process depends on the concentration of CBr_4 in the recipe. The lower degree of polymerization and the higher number of polymer chains give a lower gel content at a higher CBr_4 concentration. The fact that the sol content is lower in toluene compared to tetrahydrofuran indicates that cross-linking by hydrogen bonding is important besides the covalent cross-linking due to methylene bridge formation. From the molecular weight of the feed stage polymer, the chain transfer constant of CBr_4 to BMA is estimated to be ca. 1.06 at 70 °C. Also, the MWD of the feed stage copolymer narrows with an increase in the amount of CBr_4.

Statistical calculations based on the method of Miller and Macosko show the experimentally observed trends, although the match between the calculated and observed cross-link density values are poor. If the differences in the concentrations of cross-links calculated using the two methods (Miller–Macosko and Flory–Rehner) are attributed to physical cross-links due to entanglement, which were not accounted for in our calculations using the Miller–Macosko theory, it is evident that physical entanglements surpass chemical cross-links in their contribution to the swelling resistance of the gel. The monomer-starved semibatch process and the hydrophilicity of the NMA monomer result in a core–shell morphology of the polymer particles. This results in a nonuniform morphology of the cross-linked film. The Flory–Huggins equation cannot be used to predict the swelling of polymer gels with nonuniform distributions of cross-links, while such gels are commonly encountered during film formation from cross-linkable latexes. Some attempts to quantify the thermodynamic swelling of “inhomogeneous” gels have been described in the literature.[22,24] The NMA units of the water-soluble polymer in the latex serum can form a cross-linked membrane around the particles, hindering the interdiffusion of polymer chains between adjacent particles, during film formation and curing. The retarding effect of similar membranes on the interdiffusion of polymer chains has been investigated by Chevalier et al.[25] and Kim and Winnik.[26−28] Discussions pertaining to the morphology of the copolymer particles and films, and the kinetics of the curing process, will be presented separately. In conclusion, although the rudimentary theoretical analyses of this paper can be refined to account for the numerous complexities that we have discussed, the experimental results are expected to stimulate further research in this area.

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