Preparation and Characterization of Novel Self Cross-Linking Fluorinated Acrylic Latex

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ABSTRACT: Self crosslinking fluorinated acrylic latex (SCLFAL) has been successfully prepared via starved seeded semibatch emulsion polymerization of butyl acrylate (BA), methyl methacrylate (MMA), 2-(perfluoro-(1,1-bisisopropyl)-2-propenyl)oxyethyl methacrylate (POMA), and *N*-methylolacrylamide (NMA). The resultant SCLFAL is characterized by Fourier transform infrared (FTIR) spectrometry and nuclear magnetic resonance (NMR). Influences of the added amount of NMA on the crosslinking degree, contact angle, particle size, and glass transition temperature (T_g) of the film are investigated. Results show that the crosslinking degree, contact angle, and T_g of the film can be improved when the moderate amount of NMA is introduced into the mixed monomers. However, the added amount of NMA has no marked effect on the particle size of SCLFAL. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1997–2002, 2012

Key words: emulsion polymerization; self crosslinking fluorinated acrylic latex; preparation; characterization

INTRODUCTION

Emulsion polymers are becoming increasingly important due to their environmental compliance and are widely used in industry and can find applications in a variety of domains including water-borne adhesive, paint, and coating formulations. Fluorinated acrylate latex has both the good performance of acrylate polymer latex and fluoropolymer. It possesses the hydrophobic, oleophobic, and antifouling surface behavior. It has been widely used in the field of coatings, fabric finish, leather, and packing.[1–4]

Presently, acrylic monomers and fluorine monomers are extensively used to produce latex; and usually two or more monomers are copolymerized via a seeded semibatch approach to provide lattices with desirable properties.[5–15] However, the preparation of the self crosslinking fluorinated acrylic latices (SCLFAL) is seldom reported. In the present study, SCLFAL is prepared via starved seeded semibatch emulsion polymerizations of butyl acrylate(BA), methyl methacrylate (MMA), 2-(perfluoro-(1,1-bisisopropyl)-2- propenyl) oxyethyl methacrylate(POMA), and *N*-methylolacrylamide(NMA) (see Scheme 1). The purpose of this study was to provide self-*cross*-linking ability to fluorinated acryltate films, which are enhanced by incorporating functional moieties capable of undergoing chemical crosslinking after synthesis during film formation (see Scheme 2). Scheme 2 illustrates reactions of pendant NMA units, in one case crosslinking with an adjacent NMA unit and in the other case reacting with a hydroxyl group. We report in the following the preparation and characterization of SCLFAL. The emphasis is put in the present work on the structure and the properties of SCLFAL.
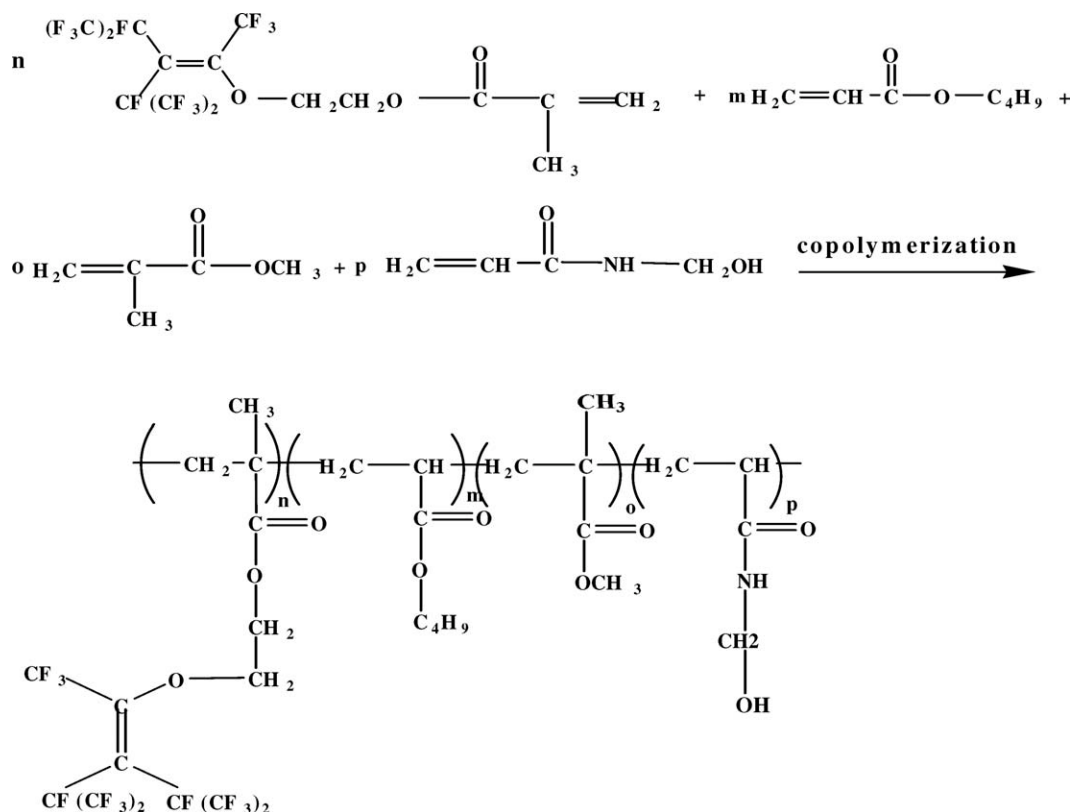
EXPERIMENTAL

Materials

Butyl acrylate (BA) and methyl methacrylate (MMA) were distilled under reduced pressure prior to polymerization. The 2-(perfluoro-(1,1-bisisopropyl)-2-propenyl)oxyethyl methacrylate (POMA) was prepared in our laboratory, which was based on our pervious work,[16] and used as received. NMA which was obtained from Shanghai Chuangxin Chemical, was used as the functional monomer. Potassium persulfate (KPS) and sodium bicarbonate (NaHCO₃) were used as received. Polyethylene glocol mono-pnonyl phenyl ether (OP-10) and sodium dodecyl benzene

Scheme 1 Reaction scheme for the copolymerization reaction of POMA, BA, MMA, and NMA.

sulfonate (SDBS) were industrial grade. The water used in this experiment was distilled followed by deionization.

Preparation of SCLFAL

All runs were performed as seeded semibatch emulsion polymerizations in three stages. The first stage was a batch seed production step, the second was a continuous stage involving feeding a monomer mixture and initiator stock solution, and the third stage was a batch finishing stage to increase the monomer conversion to completion. For the initiator stock solution, 0.90 g KPS was dissolved into 30.0 g H_2O.

The amount of KPS fed to the reaction was 2.25 parts per hundred parts monomer for all runs. The monomer emulsion stock solution consisted of 0.70 g SDBS and 2.10 g OP-10 dissolved into 110.00 g H_2O, along with 20.00 g BA, 10.00 g MMA, and 10.00 g POMA. Varying amount of NMA was added to the monomer emulsion stock solution prior to the reaction. A homogeneous aqueous solution containing 110.0 g H_2O, 0.90 g $NaHCO_3$, 0.70 g SDBS, and 2.10 g OP-10 was charged into a 250-mL four-necked flask equipped with reflux condenser, mechanical stirrer, dropping funnels, and heated with the water bath. The stirring speed was maintained at 200 rpm throughout the runs. The reactor temperature was
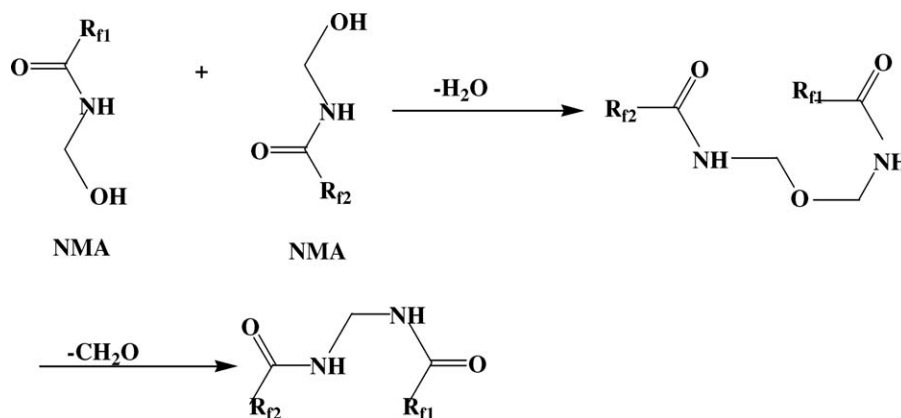
Scheme 2 Potential crosslinking reactions for NMA.

TABLE I
Recipe of Preparing SCLFAL

Ingredients	Amount/g
BA	20.00
MMA	10.00
POMA	10.00
NMA	1.50
OP-10	2.10
SDBS	0.70
KPS	0.90
$NaHCO_3$	0.90
H_2O	140.00
Conversion/%	98.73
Solid content/%	23.86

increased to 80°C within 30 min. An initiator solution containing 0.18 g KPS and 6.0 g H_2O and a monomer mixture containing 4.00 g BA, 2.00 g MMA, and 2.00 g POMA were charged to the reactor to form the seed latex within 15 min. The seeded polymerization was continued for an additional 10 min. At that point, the initiator and monomer emulsion stock solutions were added slowly to the reactor using two separate dropping funnels. The feeding time for the initiator and the monomer emulsion stock solutions were 3.5 and 3.0 h, respectively. After the feed was completed, the temperature was raised to 90°C and maintained for another 30 min to increase monomer conversion. The latex was then cooled to below 40°C, and NH_4OH (25 wt %) was added to increase the pH to about 8.0. Finally, the mixture in the flask was cooled and filtered. Thus, SCLFAL was obtained. The recipe of preparing SCLFAL was shown in Table I.

Characterizations

Fourier transform infrared (FTIR) spectrometric analyzer (Thermo Nicolet AVATAR370, USA) was used to analyze the chemical structures of the latex films. ^{19}F NMR spectrum was recorded with Bruker AVANCE III 500 MHz (Switzerland) spectrometer. $CDCl_3$ was used as internal reference for chemical shift of [19]F. ^{15}N NMR spectrum was recorded on a Varian unity 400 MHz spectrometer (10-mm probe tuned to 40.531 MHz). Thin latex film was prepared on the glass at 25°C under constant pressure. The thin latex film was put into Soxhlet extractor and extracted for 8.0 h with the solvent of benzene. The mass percentage of the residual latex film after extraction is defined as crosslinking degree. The contact angle between film and water was determined with the DataPhysics contact angle meter (OCA-20, Germany) at room temperature. The particle size, polydispersity, and ζ potential of the lattices were determined by Zetatrac dynamic light scattering detector (Microtrac Limited Corp., USA) at 25°C. The

scattering angle was fixed at 90°. The differential scanning calorimetry (DSC Q100, USA) was applied to determine T_g of the film. The heating temperature was in the range from −40 to 100°C. The heat rate was 10°C min^{-1}.

RESULTS AND DISCUSSION

Analysis of chemical structure of the latex film

Figure 1 is FTIR spectrum of the latex film of SCLFAL. In Figure 1, 2957 and 2873 cm^{-1}are the characteristic stretching peaks of C—H (CH_3,CH_2), 1731cm^{-1} is stretching vibration of C=O, 1449cm^{-1} is the skeleton vibration of C=C, which is linked with C—F bond and had relatively high stability. The wagging vibration of CH_3 is 1385 cm^{-1}, 1235cm^{-1} is the stretching vibration of C—F bonds, 1165cm^{-1} is the characteristic absorption peak of C—O in the ester group, 1066 and 842 cm^{-1} are the stretching vibration peak and wagging vibration of C—N, respectively, 753cm^{-1} is the characteristic absorption peak of C—H in BA. FTIR spectrum of SCLFAL confirms that four kinds of BA, MMA, POMA, and NMA all take part in the copolymerization reaction and SCLFAL is prepared. Figure 2 is the ^{15}N NMR of the film of SCLFAL. It indicates that the ^{15}N-peak of SCLFAL is a broad singlet from 130 to 140, agreeing with previously published chemical shifts for ^{15}N NMA.[17] Figure 3 is the ^{19}FNMR of the film of SCLFAL. It shows the following spectral data:

^{19}F NMR($CDCl_3$, δin ppm): −55.8(3F, CF_3), −70.4(6F, $CF(CF_3)_2$), −71.5(6F, $CF(CF_3)_2$), −167.5(F, $CF(CF_3)_2$), −168.8(F, $CF(CF_3)_2$). The above data also confirm that POMA has participated in the copolymerization.
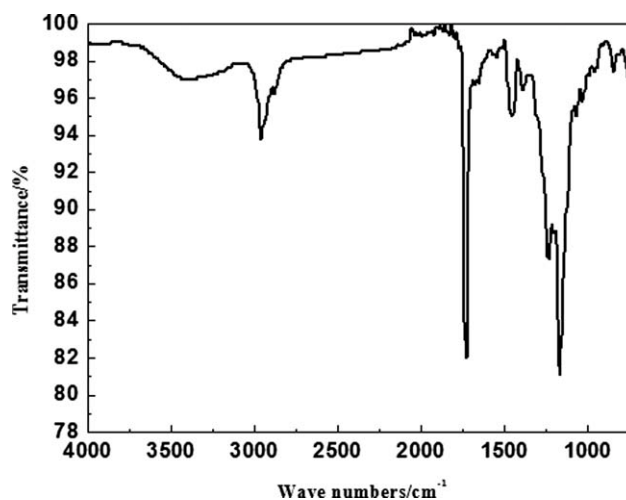

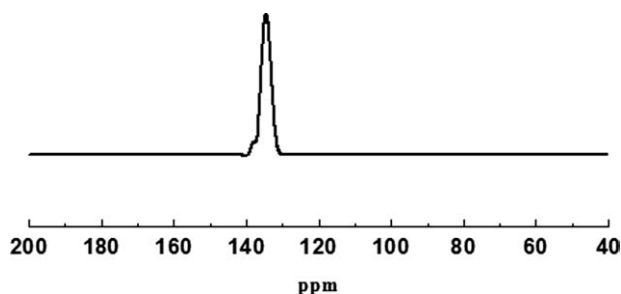**Figure 1** FTIR spectrum of the film of SCLFAL.

Figure 2 ^{15}N NMR spectrum of the film of SCLFAL.

Crosslinking degree of the film

Figure 4 is the influence of the added amount of NMA on the crosslinking of the film of SCLFAL. Figure 4 shows that the crosslinking degree is increased with the increase of the added amount of NMA when it is lower than 3.75%. NMA is copolymerized with vinyl monomer to form thermoplastic polymer since there exist two reactive functional groups in the molecular structure of crosslinking monomer, i.e., vinyl group and methylol group, which can run addition reaction and condensation reaction, respectively. There is the active methylol group in the molecular chain of the formed thermoplastic polymer. The polymer with crosslinking structure is formed after drying, dehydration, and condensation of the film. The crosslinking points are increased with the increase of added amount of NMA, leading to the increase of the crosslinking degree of the film. Figure 4 also indicates that the crosslinking degree is not increased with the increase of the added amount of NMA when it is more than 3.75%. This can be explained via the following facts. The shift of chains can be hindered by the formed network structures, which the further crosslinking reaction can be prevented.

Contact angle of the film of SCLFAL

Contact angle is a typical property to understand the surface energy of materials. The hydrophobic property of a polymeric material can be estimated in terms of contact angle measurement by depositing a water drop on the surface of film and the value of contact angle depends on the chemical compositions of film surface.[18,19] The higher the wetting resistance
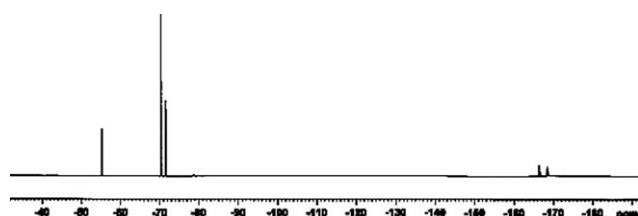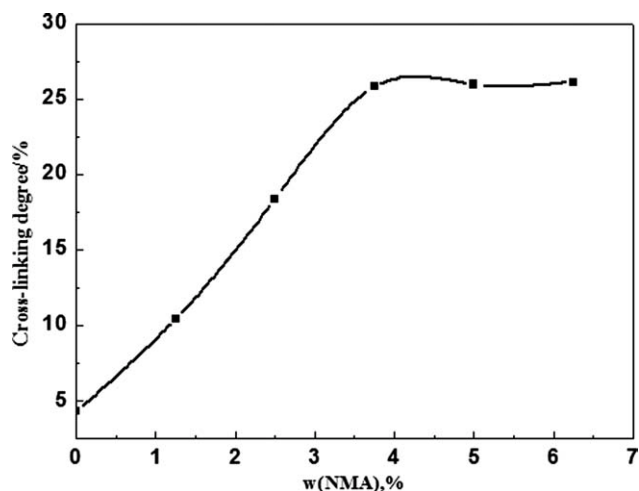

Figure 4 Influence of added amount of NMA on the crosslinking degree of film of SCLFAL.

of film surface, higher the contact angle is. The contact angles are shown in Figure 5. Figure 5 shows that the contact angle of the film is increased with the increase of the added amount of NMA when it is lower than 3.75%. Figure 5 also indicates that the contact angle of the film is decreased with the increase of the added amount of NMA when it is more than 3.75%. This is caused by the fact that the contact angle of the film is dependent on the two factors, i.e., crosslinking degree and hydrophilicity of the film. The crosslinking reaction makes the polymer turn from linear structure to network molecule. The bonding among molecular chains of the polymer is close so that small molecules are hard to penetrate into them. Therefore, the contact angle of the film is increased with the increase of the added amount of NMA. However, the hydrophilicity of the film is enhanced since NMA is introduced into the molecule of the polymer. Influence of the
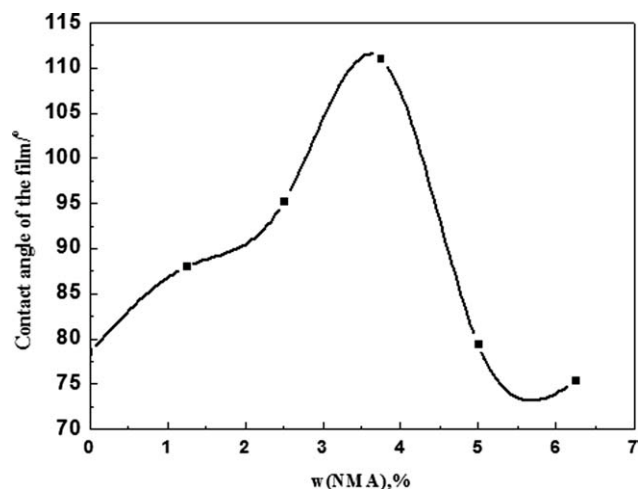

Figure 3 $^{19}FNMR$ of the film of SCLFAL.

Figure 5 Effect of the added amount of NMA on the contact angle of the film SCLFAL.
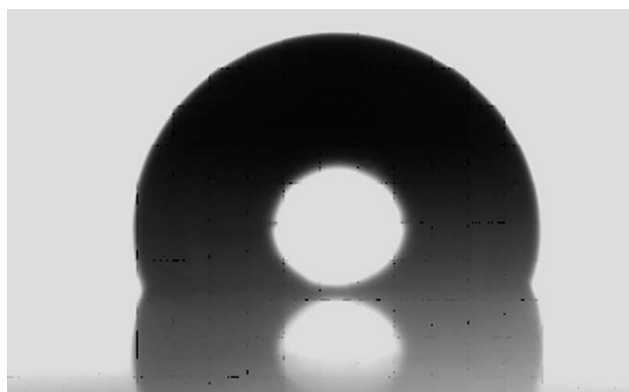
Figure 6 Maximum contact angle between SCLFAL film and water.

crosslinking and hydrophilicity of the film on the contact angle of the film has reached to the optimum equilibrium value when the added amount of NMA is 3.75%. At this time, the contact angle of the film as shown in Figure 6 is the maximum. The hydrophilicity plays a leading role in the contact angle of the film when the added amount of NMA is increased further. Thus, the contact angle of the film is decreased with the increase of the added amount of NMA when it is more than 3.75%.

Particle size and stability of SCLFAL

The particle size and ζ potential of SCLFAL are shown in Table II. Table II also shows that the added amount of NMA has no marked effect on the particle size of SCLFAL. The particle size of SCLFAL is dependent on two factors, i.e., emulsification of NMA and homogeneous nucleation. The hydrophilic group is combined with the chain of the polymer because of the polar group in NMA when NMA is copolymerized with other monomers. The hydrophilic group is arrayed on the surface of the particle of SCLFAL and forms the composite layer. At this time, NMA functions as the emulsification. Thus, the number of yielded micelles in unit volume is increased, which cause the particle size of SCLFAL to decrease. However, part of NMA is dissolved in the water phase because of its hydrophilicity. The amount of dissolved NMA is increased with the
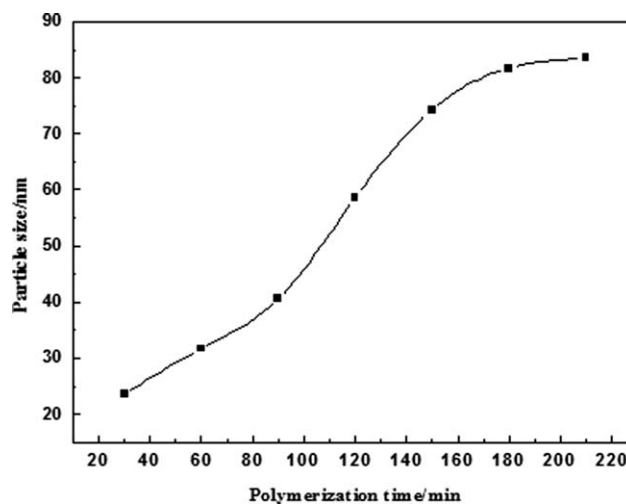

Figure 7 Variation of particle size of SCLFAL with polymerization time.

increase of the added amount of NMA. The homogeneous nucleation during the course of emulsion polymerization and the number of the formed water miscible polymer are increased. Therefore, the particle size of SCLFAL is increased with the increase of the added amount of NMA. In addition, some free radicals are consumed by homogeneous nucleation, and the probability of micellar nucleation is decreased, which prolongs the nucleation time. Thus, the number of the formed particle of SCLFAL is decreased. The particle size of SCLFAL is increased. So the particle size of SCLFAL is not changed obviously under the combined action of the above two factors. Table II also shows that ζ potential of SCLFAL is very high, which means that the repulsive force between the particles of the latex is so large that the particles do not aggregate. Thus, SCLFAL has very high stability. Figure 7 is the
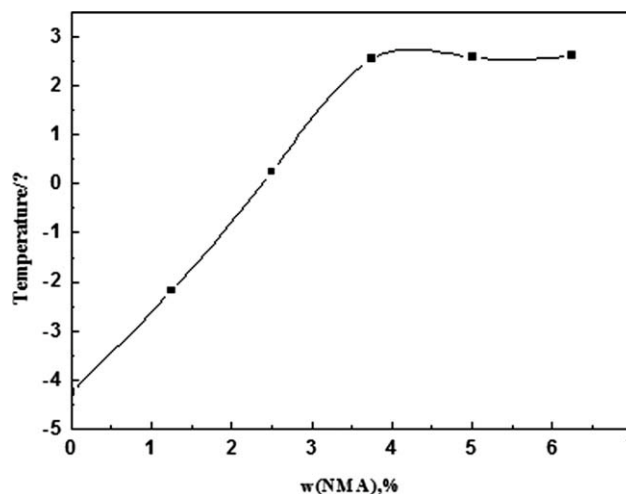
TABLE II
Particle Size and ζ Potential of SCLFAL

w(NMA), %	Particle size/nm	Polydispersity	ζ potential/mV
0	82.5	0.012	−50.82
1.25	83.1	0.031	−48.57
2.5	85.4	0.052	−47.36
3.75	83.7	0.065	−48.25
5.0	82.9	0.152	−50.54
6.25	84.3	0.168	−47.95

Figure 8 Influence of the added amount of NMA on the glass transition temperature of SCLFAL.

variation of particle size of SCLFAL with the polymerization time, where the added amount of NMA is 3.75%. Figure 7 shows that the particle size of SCLFAL is increased with the increase of the polymerization time.

Glass transition temperature

Figure 8 shows the influence of the added amount of NMA on T_g of SCLFAL. Figure 8 shows that T_g of SCLFAL is increased with the increase of the added amount of NMA when it is lower that 3.75%. This phenomenon can be explained by the following fact. The movement of the chain segment is hindered greatly with the increase of crosslinking degree when the molecular structure of SCLFAL is turned from the linear structure to network structure, thus causing T_g to increase. However, Figure 8 also shows that T_g of SCLFAL is not increased with the increase of the added amount of NMA when it is more than 3.75% which is attributed to the fact that the shift of chains has been hindered by the formed network structures, and the further crosslinking reaction has been prevented.

CONCLUSIONS

In conclusion, a novel SCLFAL was prepared successfully via starved seeded semibatch emulsion polymerization technology. That is, using BA, MMA, and POMA as the copolymerized monomers, and NMA as functional monomer, and KPS as the initiator to provide self-*cross*-linking ability to fluorinated acryltate films, which are enhanced by incorporating functional moieties capable of undergoing chemical crosslinking after synthesis during film formation. The chemical structure of the latex film is confirmed by FTIR spectrum and NMR. The crosslinking degree, contact angle, and T_g of the film of SCLFAL

can be improved when the moderate amount of NMA is introduced into the mixed monomers. However, the added amount of NMA has no marked influence on the particle size of SCLFAL.

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