

Thiol-ene emulsion polymerization using a semi-continuous approach

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Abstract

The thermally initiated thiol-ene emulsion polymerization of diallyl phthalate (DAP) diene and ethylenedioxy diethanthiol (EDDT) dithiol monomers in batch and semibatch emulsion polymerization is investigated. The batch process leads to larger and broader particle sizes than when the polymerization is carried out in semibatch. The evolution of the particle size and the final particle size distribution indicate that the stability of the latexes is limited and, hence, aggregation phenomena occurred in both processes. In particular, the evolution of the particle size distribution (PSD) in the semibatch process indicates nucleation, growth, and aggregation occurring simultaneously that produced a bimodal particle size. When the diene monomer was changed to diallyl terephthalate (DATP), the semibatch polymerization yielded smaller particles and narrow distribution without any indication of aggregation. The partial substitution of the dithiol by a trithiol monomer that is substantially more water insoluble affected nucleation of the particles, yielding for both systems smaller particles. The polythioether polymers synthesized present low glass transition temperatures ($\sim -30/-40^{\circ}\text{C}$) and those containing the terephthalate yield crystalline films. The potential application of the polymers as pressure sensitive adhesives (PSAs) was preliminarily assessed.

KEYWORDS

adhesives, batch versus semibatch, emulsion polymerization, nucleation mechanism, thiol-ene polymerization

1 | INTRODUCTION

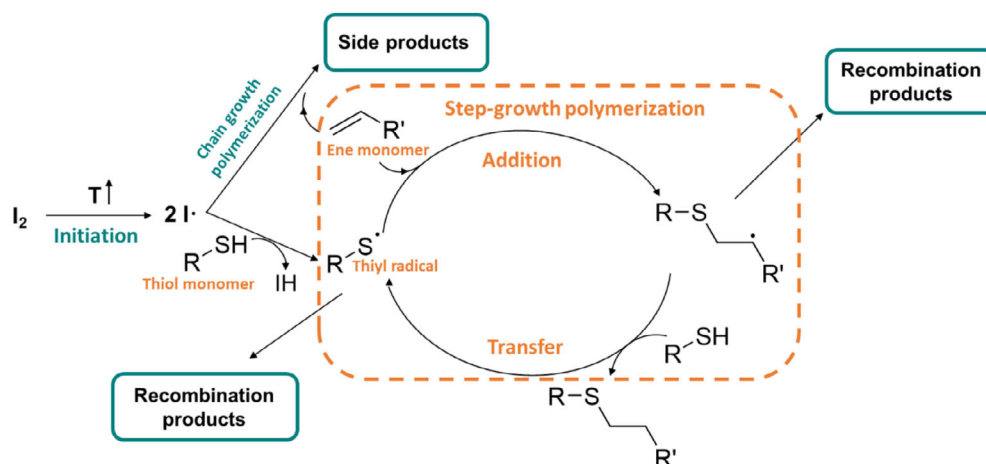
Thiol-ene polymerization is a radical step-growth polymerization process that enables the formation of polymer chains by the reaction of multifunctional thiol and ene monomers. From its step-growth polymerization nature, high conversions are necessary to achieve reasonable molar masses, and for this, keeping an equimolar ratio between the functional groups plays an important

role.^[1,2] Figure 1 presents a general scheme showing the main steps involved in thiol-ene polymerization. First, initiator radicals can abstract the hydrogen from the thiol monomer giving thiyl radicals which will then react with the ene groups of the vinyl monomers (addition) by step growth polymerization. The resulting carbon centred radical may abstract a hydrogen from another thiol molecule, giving a new thiyl radical that will propagate with another vinyl group. These addition-transfer reactions

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FIGURE 1 General scheme of radical mediated step growth thiol-ene polymerization. Figure redesigned from Derboven et al.^[3] R includes another SH chain end group and R' includes another ene chain end group.



will continue until functional thiol and ene groups are no longer available in the system. In this ideal scenario in which only addition and transfer reactions are considered, at the end of the polymerization, the number of thio-ether groups will be the same as the number of functional thiol and ene groups incorporated in the formulation if the equimolar ratio is maintained. Nevertheless, some side reactions are plausible, leading to side products which will decrease the coupling efficiency of the thiol and ene functional groups. For example, once the initiator is decomposed, the radical can react with the ene monomer by chain growth polymerization; this is more likely when homopolymerizable monomers such as acrylates are used.^[4] The consumption of the ene groups will influence the ratio of the ene and thiol functional groups. In addition, as normally multifunctional thiol and ene monomers are used, this would lead to the formation of crosslinked networks. On the other hand, termination reactions are also considered side reactions. These basically consists of the combination of different radicals; between two carbon radicals, between two thiyl radicals, or between one carbon and one thiyl radicals.

In order to have a deeper understanding of the process, several mathematical models have been developed to predict the kinetics as well as the composition of the main copolymer species formed during the polymerization process.^[3-7] Thiol-ene polymerization has been mainly explored in bulk or solution synthetic processes.^[8,9]

Reports about thiol-ene polymerizations in dispersed media are scarce.^[10] The majority of waterborne thiol-ene polymerizations described in the literature are carried out by miniemulsion polymerization. Thiol-ene miniemulsion photopolymerizations have been described for the synthesis of biomaterials,^[9,11,12] synthesis of semi-crystalline polysulphide nanoparticles,^[13,14] and synthesis of functional sub-100 nm polymer nanoparticles.^[15]

Recently, Chemtob and coworkers^[16] studied droplet nucleation during miniemulsion photopolymerization. They found out that when using water-soluble photoinitiator, substantial homogeneous nucleation was occurring even for very water-insoluble monomers. However, at small enough droplet diameters (~ 100 nm), droplet nucleation was the dominant mechanism. On the other hand, thermally initiated thiol-ene miniemulsion polymerizations were used to encapsulate different concentrations of magnetic nanoparticles for the synthesis of superparamagnetic biobased poly (thioether-ester).^[17] The encapsulation efficiency was increased by 30% through the substitution of the dithiol 1,4-butanedithiol for the tetrathiol pentaerythritol tetra (3-mercaptopropionate) (PETMP) due to the crosslinking in these nanoparticles. The nanoparticles with sizes between 95 and 260 nm presented superparamagnetic behaviour.

Notwithstanding, there are few reports of thiol-ene radical step-growth emulsion polymerization. Shipp and coworkers demonstrated that, despite the relatively small molar masses, which are typically obtained from step-growth polymerizations, emulsion polymerization of thiol-ene monomers was possible.^[18] These polymerizations were carried out in batch at small scale (10 mL) and low solids content (10 wt.%). Furthermore, bi- and trifunctional enes as well as bi- and tetrafunctional thiols were used. The effect of surfactant and initiator concentration on particle sizes was studied and an empiric correlation was obtained to predict the particle size as a function of the initiator (potassium persulphate [KPS]) and emulsifier (sodium dodecyl sulphate [SDS]) concentrations.

In a more recent publication, Chemtob and coworkers studied ab-initio batch emulsion thiol-ene photopolymerization of the dithiol ethylenedioxy diethanthiol (EDDT) and the diene diallyl phthalate (DAP) at solids contents up to 40 wt.% using 2,5 di-tert-butyl hydroquinone

(DBHQ) as inhibitor to prevent preliminary polymerization.^[19] Emulsions were prepared using a magnetic stirrer or an Ultra-Turrax homogenizer and photopolymerizations were carried out immediately after the preparation of the emulsion. Particle sizes in a range from 90 to 500 nm with relatively high polydispersities of particle size distribution were obtained. Additionally, they claimed that polymer particle formation mainly proceeded through the precipitation of oligo-radicals (*homogeneous nucleation*) even if the concentration of the emulsifier exceeded the critical micellar concentration (cmc). The same authors described the photocatalytic thiol-ene emulsion polymerization of the dithiol 2,2'-dimercaptodiethyl sulphide with various dienes.^[20] These emulsion polymerizations were carried out at a solids content of 10 wt.%. They obtained particle sizes in the range of 70–230 nm and number-average molar masses between 7500 and 1000 g/mol. Very recently, Cassidy and Shipp tried to shed light on the mechanism of particle nucleation in thiol-ene emulsion polymerization using monomers with different water solubilities, crosslinking abilities (functionality), and reactivities using SDS as surfactant and KPS as thermal initiator.^[21] They concluded that some monomer systems nucleated by heterogeneous or micellar mechanism (the ones with higher functionality) and others by homogeneous mechanism. They identify that factors like functionality and water solubility of the monomers affected the mechanism of nucleation, but they argued that the limited data available made it impossible to provide a definitive and all-encompassing model for the thiol-ene emulsion polymerization.

In this work, thiol-ene semibatch emulsion polymerization has been carried out for the first time. DAP and DATP diene monomers and EDDT dithiol monomer were used. Initially, the differences found between using batch or semibatch process are discussed. Later, semibatch emulsion polymerization of DAP/EDDT and DATP/EDDT monomer pairs with the addition of a trifunctional thiol will be compared and the microstructure of the crosslinked samples will be analyzed. In all the cases, to gain information about the nucleation mechanism through the process, particle size distributions were measured by the capillary hydrodynamic fractionation (CHDF) technique.

2 | EXPERIMENTAL PART

2.1 | Materials

DAP, Diallyl terephthalate (DATP), EDDT, and pentaerythritol tetrakis (3-mercaptopropionate) (TMPMP) monomers were purchased from Sigma-Aldrich and used without further purification (see Figure 2).

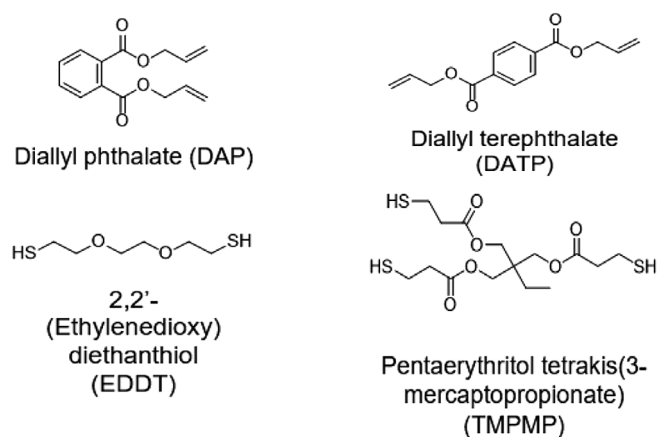


FIGURE 2 Chemical structure of the different dithiol and diene monomers used.

Dodecyl diphenyloxide disulphonate (Dowfax 2A1 45%, Dow Chemical) emulsifier and KPS (Sigma Aldrich) initiator were used as received. Hydroquinone (Sigma Aldrich) was used for stopping the reaction in the samples withdrawn from the reactor. Gel permeation chromatography (GPC) grade tetrahydrofuran (THF, Scharlab) and technical grade THF (Scharlab) were used as received for size exclusion chromatography (SEC), asymmetric-field flow-fractionation (AF4) analysis, and Soxhlet extraction (see Section 2.3 for details).

2.2 | Semibatch emulsion polymerization process

Thiol-ene emulsion polymerizations were carried out at a solids content of 25% either in a batch or in a semibatch process. For the batch polymerization, 0.012 mol of diene (DAP) and 0.012 mol of dithiol EDDT were mixed with 3 wbm% of Dowfax 2A1 as surfactant and distilled water in a 50 mL round bottom flask and under nitrogen atmosphere. The thermal initiator KPS (1 wbm%) was added dissolved in water when the reaction temperature of 75°C was reached. On the other hand, for the semibatch emulsion thiol-ene polymerizations, the surfactant Dowfax 2A1 and distilled water were mixed first in a 50 mL round bottom flask and stirred with a magnetic stirrer under nitrogen atmosphere. When 75°C was reached, the initiator was added in a shot and the addition of two feed streams was started, one with the thiol component (dithiol and trifunctional thiol in some cases) and one with the diene component (DAP or DATP), as shown in Figure 3.

The feeding of the thiol and ene monomers was done at an equimolar ratio with respect to the total amount of thiol and ene functional groups and the same amount of

FIGURE 3 Polymerization process scheme for the semibatch thiol-ene emulsion polymerizations with two different feedings. DAP, diallyl phthalate. DATP, diallyl terephthalate. EDDT, ethylenedioxy diethanthiol. TMPMP, pentaerythriol tetrakis (3-mercaptopropionate).

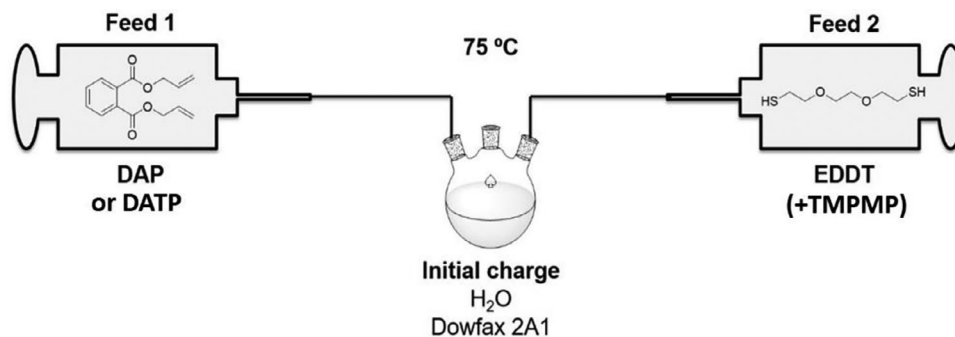


TABLE 1 Batch and semibatch thiol-ene emulsion polymerizations.

Run	Diene	Dithiol	TMPMP (%) ^a	Process
B1	DAP	EDDT	-	Batch
SB1.1	DAP	EDDT	-	Semibatch
SB1.2	DAP	EDDT	10	Semibatch
SB1.3	DAP	EDDT	20	Semibatch
SB2.1	DATP	EDDT	-	Semibatch
SB2.2	DATP	EDDT	10	Semibatch
SB2.3	DATP	EDDT	20	Semibatch

Abbreviations: DAP, diallyl phthalate; DATP, diallyl terephthalate; EDDT, ethylenedioxy diethanthiol.

^aThis percentage corresponds to the amount of thiol groups that were added with the trithiol.

reactants as in the batch process. The total feeding time was 3 h. Upon finishing the monomer addition, the reaction was kept for one more hour at the same reaction temperature. Table 1 presents all the reactions carried out. One batch experiment and six semibatch experiments were performed, not only varying the type of the diene monomer used but also including a trifunctional thiol monomer, TMPMP, which was fed together with the bifunctional thiol.

2.3 | Characterization techniques

Diene monomer conversion was followed by ¹H-NMR in a 500 MHz Bruker Avance NMR instrument equipped with a Z gradient broadband observe (BBO) probe. The ratio of the signals of the vinyl functional groups over that of the aromatic protons was used to calculate the conversion in the batch and the instantaneous conversion of the semibatch polymerization as follows:

$$X = 1 - A_{\text{vinyl}}/A_{\text{aromatic}}$$

The overall conversions for the semibatch emulsion polymerizations were calculated as follows:

$$X_{\text{overall}} = \frac{A_{\text{aromatic}} - A_{\text{vinyl}}}{A_{\text{aromatic total}}}$$

where A_{vinyl} corresponds to four protons of the double bonds ($\delta = 5.3\text{--}5.45$ ppm) and A_{aromatic} is the area of the four protons of the aromatic ring ($\delta = 7.5\text{--}7.8$ ppm) in DAP and DATP diene monomers (see Figure S1 in the Supporting Information). $A_{\text{aromatic total}}$ corresponds to the area of the aromatic groups measured to the sample after the addition of the total amount of monomer (180 min).

The polymer particle sizes were measured by dynamic light scattering (DLS) using a Zetasizer Nano Series (Malvern Instruments). The samples were diluted before the analysis and the reported average particle size values represent an average of two repeated measurements.

The evolution of the particle size distribution during the polymerizations was measured by CHDF chromatography (CHDF-2000 from Matec Applied Science). It was operated at a flow rate of 1.4 mL/min at 35°C, and the detector wavelength was set at 200 nm. The carrier fluid was 1X-GR500 (Matec). The samples were diluted to 0.6 wt.% using the carrier fluid and they were analyzed using Matec software v. 2.3.

The molar mass distribution of the polymer dispersions was measured in the following way. On the one hand, the gel fractions (or insoluble part in THF) of the crosslinked samples were measured via conventional Soxhlet extraction, using technical grade THF as solvent and calculated as shown elsewhere.^[22] The soluble fraction of the polymer was injected in a SEC apparatus. The SEC/MALS/RI equipment was composed by a LC20 pump (Shimadzu) coupled to a DAWN Heleos multiangle (18 angles) light scattering laser photometer equipped with an He-Ne laser ($\lambda = 658$ nm) and an Optilab Rex differential refractometer ($\lambda = 658$ nm) (all from Wyatt Technology Corp., USA). Separation was carried out using three columns in series (Styragel HR2, HR4, and

HR6; with pore sizes from 10^2 to 10^6 Å). Filtered toluene (HPLC-grade from Sigma-Aldrich) was used for the calibration of the 90° angle scattering intensity. The detectors at angles other than 90° in the MALS instrument were normalized to the 90° detector using a standard (PS 28,770 g/mol, Polymer Labs) which is small enough to produce isotropic scattering at a flow rate of THF through the detectors of 1 mL/min. In addition, the same standard and conditions were used to perform the alignment (interdetector delay volume) between concentration and light scattering detectors and the band broadening correction for the sample dilution between detectors.

The analyses were performed at 35°C and THF was used as mobile phase at a flow rate of 1 mL/min. For the SEC analysis, the soluble polymer recovered from Soxhlet extraction was dried and diluted in HPLC grade THF at concentrations of 5–10 mg/mL and then were injected into the equipment. The SEC/MALS data was analyzed by using the ASTRA software version 6.1 (Wyatt Technologies, USA).

In addition, asymmetric-field flow-field fractionation (AF4, Wyatt Eclipse 3) using the same eluent, pumping, and detector system as for the SEC analysis was used to analyze the whole polymer sample. 10 mg of the latices were dispersed in 1 mL of THF for the preparation of the samples. 50 μL of this dispersion was injected for the measurement. The Debye plot with second-order Berry formalism was used to calculate the molar mass from the RI/MALS raw data.

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC, Q1000, TA Instruments) of dry polymers from the final latexes using hermetic pans.

Probe tack tests were performed on glass plates according to ASTM-D2979. Films were cast from the latexes and dried for 12 h before the measurements were carried out. A 1 in. stainless steel ball was moved downwards to the film with a speed of 0.1 mm/s and brought into contact with the PSA film for a contact time of 1 s. Thereafter, the stainless steel ball was moved upwards at a speed of 0.055 mm/s until either a cohesive or adhesive failure was observed so that the probe was completely separated from the PSA film.

3 | RESULTS AND DISCUSSION

As has been mentioned in the introduction, few reports have been published related to thiol-ene emulsion polymerization and all of them were carried out batchwise. In this work, semibatch thiol-ene emulsion polymerization was explored and compared to a batch processes. The thiol-ene monomer system used in this work was as the one reported by Chemtob and coworkers^[19] (DAP and

EDDT), using thermal initiation instead of photoinitiation and at a higher solids content. The monomer ratio was equimolar and the surfactant concentration was above the cmc in all cases.

High vinyl group conversions were achieved in both cases at the end of the polymerization with final conversions of 98% for the batch system and 99% for the semibatch one. Furthermore, Figure 4A shows that in the batch process, very high conversions (above 90%) were reached at very early stages of the polymerization, whereas in the semicontinuous reaction, monomer starved conditions were achieved with instantaneous conversions above 90% during the whole addition period.

The final particle size measured by DLS for the batch process (519 nm) was slightly larger and the dispersity broader (PDI = 0.2) than for the semibatch experiment (470 nm and PDI = 0.1). However, the evolution of the particle size was different, as shown in Figure 4B. In the batch experiment, the particle size measured at short reaction times likely corresponds to droplets (above 1 μm) and quickly decreased below 600 nm, and after 50 min of reaction remained constant because the reaction was mostly completed at shorter times. For the semibatch process, the initial particles are notably smaller (200 nm) and grew in size as monomer was fed to the reactor, reaching larger sizes at the end (see the discussion below with the help of particle size distribution [PSD] evolution). The final particle size was also measured by CHDF (see Figure 4C). Broad particle size distributions were obtained in both processes, but substantially higher in the batch process with particles in the range of 100–800 nm, whereas in the semibatch process, particles between 100 and 500 nm were produced.

The evolution of the number of particles for each experiment was determined from the average particle size and it is plotted in Figure 4B (squares). Since the polymerization rate was very fast in the batch process and the particles were created by the first 10 min of reaction, it can be speculated that nucleation and aggregation processes simultaneously occurred, leading to the broad distribution measured after 250 min. The number of particles was maintained roughly constant during the reaction because most of the monomer had already reacted by the first 50 min. On the other hand, for the semibatch experiment (SB1.1), it can be seen that N_p increases steadily up to the end of the feeding time. In the postpolymerization stage, there is some particle aggregation leading to a decrease of the number of particles. The evolution of the PSD along the reaction was measured, and it will be discussed below when comparing the evolution for the experiments of the DATP/EDDT systems. The lower particle size achieved in the initial

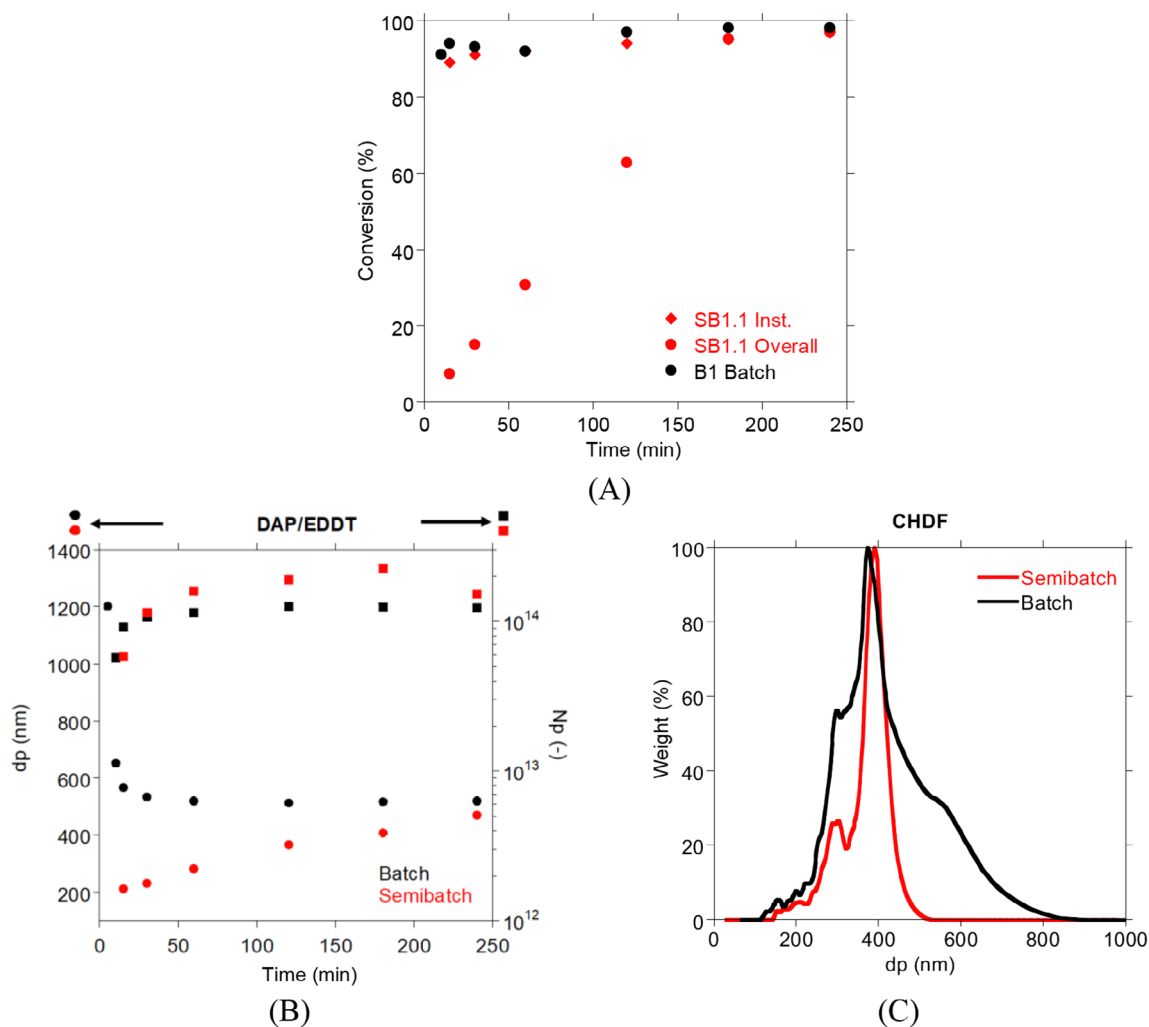


FIGURE 4 (A) Time-evolution of the instantaneous and overall conversion of diene for the semibatch diallyl phthalate/ethylenedioxy diethanthiol (DAP/EDDT) emulsion polymerization (SB1.1) and diene conversion for the batch emulsion polymerization of DAP/EDDT (B1); (B) Intensity-average particle sizes (circles) measured by dynamic light scattering (DLS) and number of particles (squares). (C) Particle size distribution measured by capillary hydrodynamic fractionation (CHDF) for both batch and semibatch thiol-ene emulsion polymerizations.

stages of the reaction in semibatch can be likely attributed to the lower polymerization rate as a consequence of the lower monomer concentrations. It is likely that the sizes of the primary particles in both processes were similar (the same nucleation mechanism), but in the batch process, aggregation of the polymer particles occurred quickly, while in the semibatch process, particles grew because the monomer that was fed was preferentially incorporated into the polymer particles. Nonetheless, it cannot be ignored (as shown below) that aggregation also took place along the feeding period.

The final molar mass of the SB1.1 latex was small (34 kDa, see Table 3), which limits the potential applications of these latices. In order to increase molar masses and hence mechanical properties, a trifunctional thiol monomer was incorporated into the semibatch

formulation. Furthermore, another diene monomer, DATP, was also considered (see chemical structure in Figure 1). The trifunctional thiol TMPMP was fed in the same stream as the thiol component and the ratio of vinylic and thiol functional groups was kept at 1:1. Two different TMPMP monomer concentrations were analyzed for both DAP/EDDT and DATP/EDDT monomer pairs: 10% and 20%. This percentage corresponds to the amount of thiol groups that were added with the trifunctional thiol.

For all the polymerizations presented in Table 2, no matter the TMPMP content, the diene conversion was almost complete at the end of the process. It can be observed that, in both cases, the final particle size was smaller when the trifunctional monomer was incorporated into the system. Nevertheless, the size of the particles was larger for the DAP/EDDT system than for the DATP/EDDT.

TABLE 2 Characteristics of the latexes synthesized by semibatch emulsion polymerization of diallyl phthalate (DAP)/ethylenedioxy diethanthiol (EDDT) and diallyl terephthalate (DATP)/EDDT with different pentaerythriol tetrakis (3-mercaptopropionate) (TMPMP) concentration. Conversion (X), particle size (dp), polydispersity index (PDI), glass transition temperature (T_g), and melting temperature (T_m) are shown.

	Run	TMPMP (%)	X (%)	dp (nm)	PDI	T_g (°C)	T_m (°C)
DAP/EDDT	SB1.1	0	99	470 ± 1.9	0.1	-40	-
	SB1.2	10	99	213 ± 1.6	0.04	-34	-
	SB1.3	20	98	212 ± 1.9	0.01	-32	-
DATP/EDDT	SB2.1	0	99	193 ± 1.1	0.02	-36	51
	SB2.2	10	98	123 ± 1.4	0.07	-32	53
	SB2.3	20	97	122 ± 1.6	0.03	-31	49

TABLE 3 Weight-average molar masses determined by SEC/MALS (low molar mode) and AF4/MALS/RI (high molar mass mode) and gel contents measured by Soxhlet extraction (GC Soxhlet).

Run	GC Soxhlet (%)	Low mw mode (kDa)		High mw mode (kDa)	
		\bar{M}_w	\bar{M}_n	\bar{M}_w	\bar{M}_n
SB1.1	0	34	1.5	-	-
SB1.2	21	50	5.8	880,700	1.00
SB1.3	11	241	7.2	1,363,000	1.01
SB2.1	0	39	1.9	-	-
SB2.2	24	21	3.2	296,400	1.00
SB2.3	38	11	2.1	334,700	1.04

Figure 5A displays the instantaneous and overall conversions for the two runs carried out without the trifunctional thiol: SB1.1 and SB2.1, respectively. It can be seen that starved conditions were achieved during the whole polymerization process. Figure 5B–E presents the evolution of the particle size and the number of particles along the reaction, and Figure 6 shows the evolution of the particle size distribution for the experiments carried out in absence of trithiol monomer for both DAP/EDDT and DATP/EDDT systems. For the DAP/EDDT system, the initially nucleated particles were larger in the absence of the TMPMP trithiol monomer. Particle growth was similar for systems with and without TMPMP, although the experiments with trithiol did not suffer aggregation during the postpolymerization stage (note that particle sizes in SB1.2 and SB1.3 experiments overlap). This difference in the size of the initially nucleated particles is not understood yet, but it should be related with the lower water solubility of the trithiol monomer (monomer solubilities are: TMPMP = 3.69 mg/L, DAP = 43 mg/L, DATP = 33 mg/L, and EDDT = $11 \cdot 10^3$ mg/L).

For the DATP/EDDT system, the particle sizes are smaller than for the DAP/EDDT system no matter

whether TMPMP was used (SB2.2 and SB2.3) or not (SB2.1). As observed for the DAP/EDDT system, the amount of TMPMP (10 or 20%) had little effect on the evolution of the particle size. In the experiments where TMPMP was added (SB2.2 and SB2.3), the particles grew in size, but the growth was modest compared with the case without TMPMP (SB2.1).

In order to better understand the difference in the particle size of the experiments carried out without the TMPMP (SB1.1 and SB2.1), the particle size distribution was measured by CHDF during polymerization (see Figure 6).

The particle size distribution was much broader (indeed, the final PSD is bimodal) for the DAP/EDDT system than for the DATP/EDDT system. In addition, for the DAP/EDDT system, it can be seen that at the beginning of the polymerization (15 min), a single and relatively broad population of particles centred at around 200 nm was produced. This population of particles grew in size by the monomer fed to the reactor. Nevertheless, the PSD tails toward the low particle size, and above a certain time, the PSD shows a bimodal distribution with a small fraction of particles at 300 nm and the main population, formed by the growth and aggregation of the initially created particles, at 400 nm.

This indicates that a continuous particle nucleation, growth, and aggregation took place during the polymerization. For the DATP/EDDT system, the evolution of the PSD was different. First, as discussed above, the particles nucleated at the beginning of the polymerization were smaller (particle sizes below 100 nm), and during the process, these particles grew in size (by the addition of the monomer) with no indication of creation of new particles or aggregation (see Figure 6B); as can be seen in Figure 5E, the number of particles is roughly constant. The reason for the larger particle size obtained at the initial stages of the semibatch process for DAP/EDDT monomer pair is not well understood and requires further research.

The molar mass distribution of the latexes was analyzed by SEC/MALS/RI for the two latexes without the

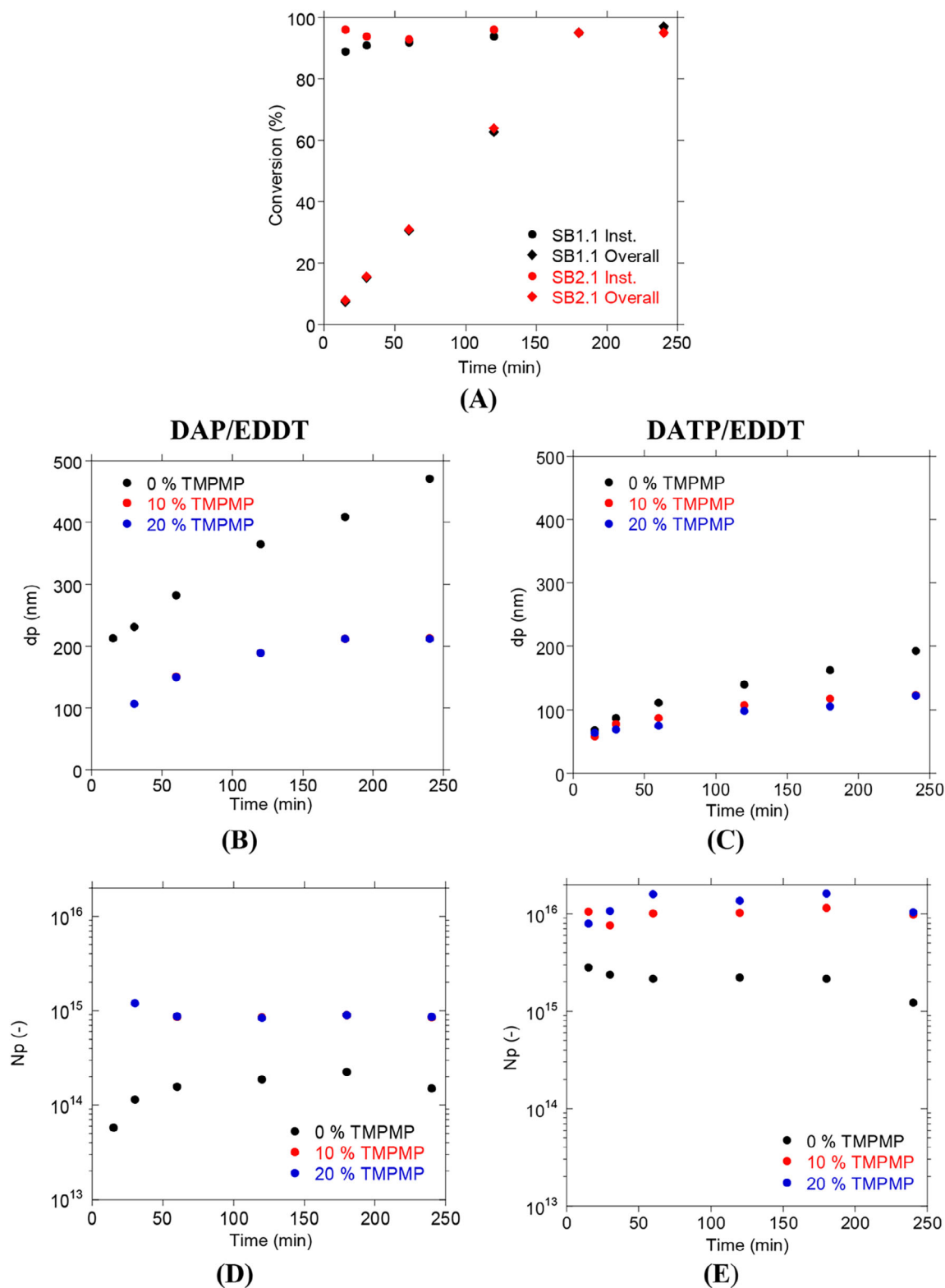


FIGURE 5 (A) Instantaneous and overall conversions for runs SB1.1 and SB2.1. Evolution of particle sizes and number of polymer particles during the semibatch emulsion polymerization of diallyl phthalate (DAP) and ethylenedioxy diethanthiol (EDDT) (B and D) and diallyl terephthalate (DATP) and EDDT (C and E) with different amounts of the trifunctional thiol pentaerythritol tetrakis (3-mercaptopropionate) (TMPMP).

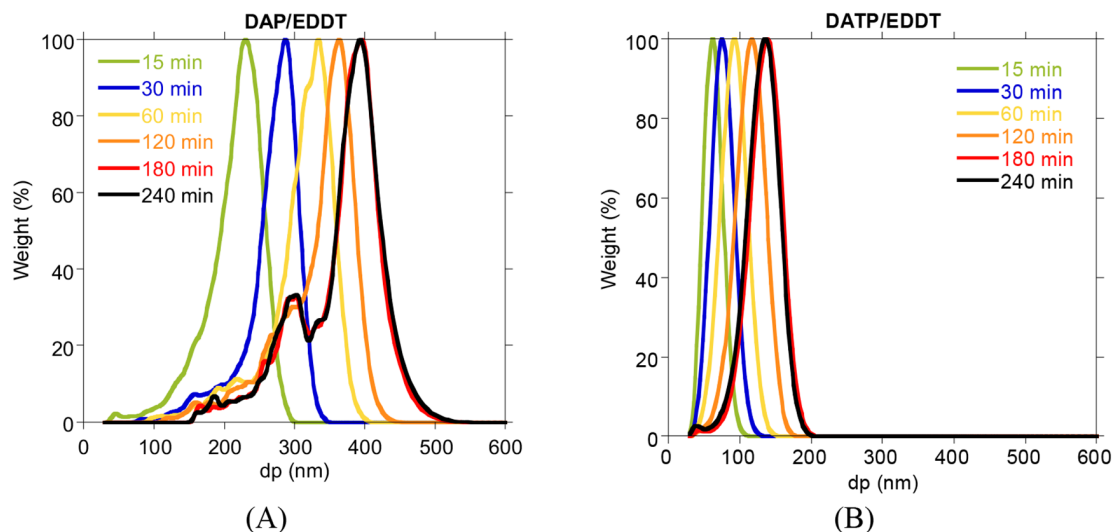


FIGURE 6 Particle size distribution evolution measured by capillary hydrodynamic fractionation (CHDF) for (A) diallyl phthalate/ethylenedioxy diethanthiol (DAP/EDDT) 0% pentaerythriol tetrakis (3-mercaptopropionate) (TMPMP) (SB1.1) reaction and (B) diallyl terephthalate (DATP)/EDDT 0% TMPMP (SB 2.1).

trifunctional thiol. The latexes with 10% and 20% of TMPMP were not completely soluble in THF, and hence only the soluble fraction after Soxhlet extraction was measured. The non-soluble fraction of these samples was considered as gel polymer and reported as gel content in Table 3. Additionally, each latex sample was injected into an AF4/MALS/RI apparatus in an attempt to obtain information of the entire molar mass distribution in a single analysis. Unfortunately, it was not possible to find a crossover flow that would allow for the separation of the two populations of chains with enough sensitivity in the light scattering detector (see Figure S2 in the Supporting Information) for the small population of chains. Therefore, the molar mass obtained by AF4/MALS/RI corresponds to the high molar mass mode (i.e., the insoluble fraction or gel content).

Overall, Table 3 shows that, as expected, when increasing the TMPMP content, the gel content increased. Experiment SB1.3 did not follow this trend; that is, the gel content was lower than for SB1.2 in which a higher trifunctional monomer amount was used in the formulation. This was not expected, but the fact that the soluble fraction has a broader distribution ($\text{Đ} = 7.2$) and a much larger average molar mass (241 kDa) is coherent with a higher concentration of trithiol monomer. Furthermore, the molar mass of the gel is larger too. The average molar masses of the soluble fraction for the series DATP/EDDT decreased with increasing concentration of trithiol as one would have expected by the higher amount of gel obtained at increased concentrations of TMPMP. The high molar mass mode for the crosslinked samples (SB1.2, SB1.3, SB2.1, and SB2.3) indicated the formation of

extremely high molar masses for both systems, higher for the DAP/EDDT system, and that it was caused by the high concentration of trithiol monomer employed in the polymerizations that created a very crosslinked polymer network. The molar masses obtained in these reactions are limited by the size of the particle and this explains why the molar masses for the DAP/EDDT system are higher. The molar mass values approached the maximum molar mass of a single crosslinked chain in particles with the particle sizes reported in Table 2 ($3 \cdot 10^9$ Da for particles with 215 nm and $5.4 \cdot 10^8$ Da for particles around 120 nm).

The glass transition temperatures (see Table 2) increased from -40 to -32°C when increasing TMPMP concentration for runs of SB1 and from -36 to -31°C for runs of SB2. Furthermore, the latexes containing DATP as the diene monomer contained crystalline domains, as melting peaks were observed around 50°C for the three cases. It seems that the *para*-substituted diene monomer DATP might induce crystallization, which could be attributed to the linear polymer structured formed. Further DSC measurements were carried out to the dried polymers to confirm the presence of the crystalline domains, and two heating cycles were done for each sample containing DATP monomer (see Figure S3 in the Supporting Information). The melting peak was only visible in the first cycle and, therefore, the second-order transition of the glass transition temperature was more pronounced in the second heating cycle. These results indicate that the polymer contained crystalline domains during the first cycle and behaved completely as an amorphous polymer in the second heating cycle as was recently reported by Le et al.^[20] The crystallization

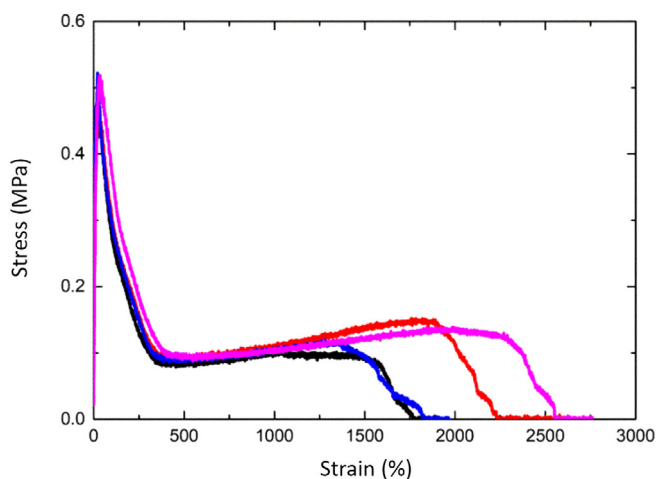


FIGURE 7 Probe tack curves of the dried film of the latex of diallyl phthalate (DAP) and ethylenedioxy diethanthiol (EDDT) with 10% of pentaerythriol tetrakis (3-mercaptopropionate) (TMPMP).

kinetics were slow because of the rigidity of the polymer chains provided by the phenyl group; therefore, once the crystalline domain was molten after the first heating cycle in the DSC, the polymer did not recrystallize within the time of the cooling ramp. The same behaviour was found for all of the samples containing DATP, in which the melting peak was only visible in the first DSC cycle. The glass transition temperature shifted when increasing TMPMP content to slightly higher temperatures (see Figure S4). However, the melting temperature did not show a trend depending on the TMPMP content.

One of the potential applications of the thiol-ene emulsion polymers that present T_g s in the range of -30 to -40°C (and contain degradable polyesters in the backbone) is as PSA. Therefore, films were cast at room temperature (23°C) and probe-tack measurements were carried out to preliminarily assess their adhesive performance. The three DAP/EDDT formulations, with and without the TMPMP trifunctional monomer, presented tacky properties. Thus, the DAP/EDDT system with 10% of TMPMP trifunctional thiol monomer, SB1.2, was considered as an example to assess its adhesive performance. Films with a thickness of $100\ \mu\text{m}$ were prepared on a glass substrate and probe tack was measured. The dried film of this latex was not completely homogeneous and, therefore, probe tack measurements were carried out in different locations of the film. Each curve in Figure 7 belongs to a measurement in a different position of the film. Even if the measured strains are very different depending on the location of the measurement (between 1800% and 2500%), the stress-strain curve was representative of PSA.^[23]

Overall, the mentioned strain is high and the curves present a plateau, which is characteristic of the fibrillation

process. Therefore, improving the film formation process to get homogenous films and optimizing the formulation (by adjusting the TMPMP concentration and hence control the molar mass distribution), this type of material can be a good candidate for PSA applications.

4 | CONCLUSIONS

The thiol-ene emulsion polymerization of two thiol-ene systems, DAP/EDDT and DATP/EDDT, in the absence and presence of a trithiol monomer (TMPMP) has been studied. First, batch and semibatch processes were compared for the DAP/EDDT system. It was found that the batch process yields larger particles and a broader PSD than the semibatch. From the evolution of the particle sizes and the final PSD of the latexes, it can be concluded that the stability of the latexes (Dowfax 2A1 surfactant employed) was limited and aggregation of the particles occurred in both cases, yielding broad PSD.

The semibatch reactor was further used by adding a trithiol monomer in the formulation and by replacing the diene (DATP instead of DAP). Interestingly, it was found that by only changing the diene, the stability of the latexes substantially improved, avoiding aggregation and obtaining smaller particles with narrower PSD for the DATP/EDDT system.

When the trithiol monomer was partially incorporated into the formulation replacing EDDT, the polymerizations yielded smaller particles in both systems although, the amount of trithiol did not affect the particle size. This was not expected, and it demonstrates how sensitive the nucleation of polymer particles in the thiol-ene emulsion polymerization is. The different water solubilities of the monomers (EDDT is water soluble, whereas DATP and DAP are one order of magnitude less water soluble than styrene, and TMPMP is the most insoluble of all the diene monomers) likely play an important role in how nucleation takes place. This finding was recently reported by the works of the groups of Chemtob^[19] and Shipp,^[21] which recognize that the nucleation in thiol-ene emulsion polymerization is still not well understood and hence requires additional research to be conducted in the following years.

On the other hand, all the polythioether polymers synthesized presented glass transition temperatures below room temperature ($\sim -30/-40^\circ\text{C}$), making them potentially good candidates for PSA applications. The probe tack curve was assessed for one system and it showed a typical fibrillation plateau required in PSAs, and although still far from a waterborne acrylic PSA, it may be possible to optimize the microstructure of the polythioether polymers to improved their adhesion performance. Furthermore, although not assessed in this work, the polythioether

polymers synthesized bear in their structure ester units that can be degraded and, therefore, this might allow the production of more sustainable adhesives.

AUTHOR CONTRIBUTIONS

Fabian Wenzel: Formal analysis; investigation; writing – original draft. **Urko Larrañaga:** Data curation; investigation. **Miren Aguirre:** Data curation; supervision; writing – original draft; writing – review and editing. **Jose R. Leiza:** Conceptualization; data curation; funding acquisition; methodology; resources; supervision; validation; writing – review and editing.

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PEER REVIEW

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DATA AVAILABILITY STATEMENT

Data available upon request from the authors

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SUPPORTING INFORMATION

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