

# Styrenation of Linseed Oil by NMRP-mediated Miniemulsion Polymerization

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**Abstract:** In this study, triglyceride oil-styrene copolymerization was carried out with nitroxide mediated radical polymerization (NMRP) technique in miniemulsion medium. For this purpose, firstly, 4,4'-azobis-4-cyanopentanoyl chloride (ACPC) was synthesized from 4,4'-azobis-4-cyanopentanoic acid (ACPA). Macroazoinitiator which comprises thermally labile azo groups was obtained with reaction of partial glycerides (PGs) and ACPC. Then, oil-based macroazoinitiator and styrene mixture was subjected to styrenation in the presence of nitroxide radical 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO) in order to obtain styrenated oil product with low polydispersity index (PDI) in miniemulsion medium. Miniemulsion mixture was prepared by ultrasonication process by using DOWFAX 8390 and hexadecane (HD) as surfactant and costabilizer, respectively. Miniemulsion polymerization was carried out at different surfactant concentrations in order to determine the ideal surfactant concentration. For this purpose, droplet/particle sizes were measured throughout the reaction and the surfactant amount for the least change in droplet/particle size was determined. Products obtained by ideal process were characterized by FT-IR, <sup>1</sup>H-NMR and GPC measurements. Styrenation process was also performed by solution polymerization in xylene for the purpose of comparison with the miniemulsion medium. It was understood that, styrenation process carried out successfully with NMRP adapted miniemulsion polymerization because colloidal stability could be achieved. Film properties of styrenated oil samples were determined to related standards. The obtained styrenated oil samples showed good film properties and could be used as a coating material.

**Keywords:** Miniemulsion, NMRP, linseed oil, binder, styrenated oil.

## I. INTRODUCTION

In this study, styrenated oil preparation was performed by nitroxide mediated radical polymerization (NMRP) in miniemulsion because of its benefits over classical emulsion polymerization. Since the ingredients of the polymerization carried out in this study were water insoluble, their incorporation into the polymer structure was favoured under miniemulsion condition. In this way, it was aimed to prevent homopolymerization of styrene, which occurs in classical styrenation process [1-4]. Actually, in order to prevent the homopolymer formation in styrenated oil production, previously a number of studies were completed in our laboratory [5-16]. In this context, macroinitiator [5-9] and macromer [5-12] techniques were developed and applied in solution polymerization. These strategies were also successfully performed in the case of controlled living radical polymerization (CLRP) such as NMRP [13, 14] and reversible addition-fragmentation chain transfer (RAFT) polymerization [15, 16] in solution, and styrenated oil samples with low polydispersity index (PDI) and good film properties were obtained.

Recently, CLRP techniques such as ATRP, NMRP and RAFT have been widely used in the synthesis of complex macromolecules with low molecular weight distribution and pre-estimated molecular weights [17-27]. Researches

on NMRP technique were focused on homogeneous systems such as solution and bulk polymerizations and were successfully applied [21-27]. In early applications of NMRP in macroemulsion system were not so successful, because preservation of the living characteristics of the polymerization and elimination of the oversized particles could not be achieved [28]. These unsuccessfulness was due to the using unsuitable surfactants and nitroxide components in the macroemulsion polymerization. Since NMRP is realized relatively at a high temperature (120-135 °C), the traditional surfactants such as CTAB, SDS decomposed and caused colloidal instability [28].

Additionally, the solubility of nitroxide component in water and oil phases should be suitable for the applied polymerization. Otherwise the polymerization cannot be controlled [28, 29]. Since the surfactants such as DOWFAX 8390 and SDBS are more stable at temperature about 135 °C, they were used in the later studies on NMRP macroemulsion polymerization [28-37]. In order to have a good colloidal stability, apart from surfactant, unimer initiating systems were also investigated instead of bicomponent initiating system [28, 32, and 33]. In the case of unimer, initiator is even at the beginning in the oil droplet, the polymerization occurs to a great extent in droplets [28, 32, and 33].

In literature, oil and alkyd based systems with different acrylic combinations were used for preparation of waterborne binder. Heiskanen and co-workers studied preparation of alkyd-acrylic hybrids in the presence of unsaturated resin by classical emulsion polymerization. Their results showed that the film properties of alkyd-acrylic products such as drying, penetration and water repellency ability were improved [38]. Van Es et al. studied oil-acrylate polymerization in miniemulsion condition. In their study, hydroperoxides of triglycerides and t-butyl hydroperoxide were used as an initiator and reactions are carried out with same redox system (Fe (II)/EDTA/SFS). Their results showed that polymerization reaction which is initiated by hydroperoxides of triglycerides resulted in homogenous particle while t-butyl hydroperoxide initiated system caused to phase separation [39]. Schork and co-workers studied alkyd-acrylate polymerization in miniemulsion condition. They carried out the polymerization reactions by using linoleic acid and sunflower seed oil and improved the homogeneity of hybrid particles [40]. In another study, Schork et al. carried out copolymerization of alkyd-acrylates in emulsion and miniemulsion conditions. It was understood that miniemulsion system was more effective compared to classical emulsion polymerization because of mass transport limitations of the alkyds in emulsion system [41].

Uschanov and co-workers used conjugated and non-conjugated tall oil fatty acids-based alkyds in miniemulsion polymerization of alkyd-acrylates. Polymerization reactions were carried out with different alkyd-acrylate ratio and they noticed that the polymerization rate decreased with higher alkyd content. As a result, it was understood that the grafting procedure was more dependent on acrylate structure than alkyd resin. The degree of grafting was not influenced by alkyd resin type [42].

In the current study, copolymerization of oil and styrene was performed under miniemulsion conditions. In this way, it was aimed to eliminate the problems of colloidal instability, to a great extent, encountered in macroemulsion polymerization. It is well known that in miniemulsion polymerization the droplets are so small that they compete for the radical entry and, consequently, they become a 'nanoreactor' where the polymerization takes place [43, 44]. In this study, a new strategy was applied for determining the best conditions for miniemulsion polymerization.

In order to understand whether the polymerization was miniemulsion or not, in literature, the widespread way was to measure the droplet/particle size at the beginning and/or at the end of the polymerization. If the droplet/particle size was within the size of the miniemulsion, polymerization was accepted as a miniemulsion polymerization [45-50]. However, this procedure cannot guarantee that the polymerization is carried out under ideal conditions for miniemulsion polymerization. By taking this fact into account, we applied a new strategy based on determining

the conditions ensuring that the droplet/particle sizes remain practically unchanged during the polymerization. In other word, by applying this strategy, the conditions of being 1:1 copy for the droplets [28, 34] throughout the polymerization were determined. Finally, styrenated oil sample which was prepared under the determined ideal miniemulsion conditions was investigated in view of molecular weight, PDI and film properties. The styrenated oil thus obtained had a molecular weight distribution lower than that of classical NMRP polymerization in solution. In the end, film properties of the styrenated oil samples were determined. The results showed that the prepared styrenated oil products could be used successfully as an oil based binder.

## II. EXPERIMENTAL

### A. Materials

Styrene (St, 99%, Aldrich) was passed through a column to remove the inhibitor. Commercially purchased linseed oil was used as for PG preparation. Methanol ( $\geq 99.8\%$ , Sigma-Aldrich), ethanol ( $\geq 99.5\%$ , Sigma-Aldrich), diethyl ether ( $\geq 99\%$ , Sigma-Aldrich), toluene ( $\geq 99.8\%$ , Sigma-Aldrich), glycerol ( $\geq 99.5\%$ , Merck), sulphuric acid (95-98%, Merck), pyridine ( $\geq 99.8\%$ , Sigma-Aldrich), potassium hydroxide ( $\geq 85\%$ , pellets, Sigma-Aldrich), benzene (anhydrous,  $\geq 99.8\%$ , Sigma-Aldrich) and tetrahydrofuran (THF,  $\geq 99.9\%$ , HPLC grade, Sigma-Aldrich) were used as received. 4,4-Azobis(4-cyanopentanoic acid) (ACPA) was used as received.

DOWFAX 8390 and hexadecane (HD, co-stabilizer, Sigma-Aldrich) were used without further purification. 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) (99%, Sigma-Aldrich) was used as received. Thionyl chloride ( $\geq 99.0\%$ , Sigma-Aldrich) was used as received for synthesis of 4,4-Azobis(4-cyanopentanoic acid) (ACPC). Dichloromethane (anhydrous,  $\geq 99.8\%$ , Sigma-Aldrich) was used as reaction medium for ACPC synthesis. Xylene (anhydrous,  $\geq 99.8\%$ , Sigma-Aldrich) was used as reaction medium for solution polymerization reactions. Lead naphthanate (0.5%) and cobalt naphthenate (0.05%) were used as drier for film applications.

### B. Characterization

The Fourier-Transform infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer for structure analysis.  $^1\text{H-NMR}$  spectra were recorded on an Agilent NMR System VNMR5 500 spectrometer at room temperature in  $\text{CDCl}_3$  with  $\text{Si}(\text{CH}_3)_4$  as an internal standard for structure analysis. The droplet and particle size distributions for copolymer samples were monitored by dynamic light scattering (DLS, Zetasizer 4000, Malvern) system. The molecular weight and molecular weight distributions of the resulting polymers were determined by gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran (THF) as the eluent at a with molecular weight ranging from 580 to  $355,000 \text{ g mol}^{-1}$ .

### C. Preparation of Partial Glycerides

Partial glycerides (PGs) were obtained by glycerolysis reaction between triglyceride oil and glycerol. Linseed oil (200 g) and glycerol (17 g) were placed in a three necked reaction flask and heated. When the temperature reached to 218 °C, 0.2 g calcium hydroxide (0.1%, by weight to oil portion) was added to the mixture as catalyst. After the catalyst addition, nitrogen was passed through the reactor for 5 min. When the temperature reached to 230 °C, the reaction was continued for 1 h at this temperature.

Samples taken from the reaction mixture were added to ethanol and when the ethanol phase became clear, reaction was terminated. Then glycerolysis product was cooled and dissolved in diethyl ether. The mixture was placed in a separatory funnel and washed with sulphuric acid (0.2 N) to remove catalyst and then washed with distilled water to remove sulphuric acid and free glycerol. The solution was dried overnight with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, diethyl ether was removed by rotary evaporator and then hydroxyl and acid values of product were determined by related procedures [51].

### D. Synthesis of 4,4'-azobis(4-cyanopentanoic chloride) (ACPC)

ACPA was dispersed in 150 ml dichloromethane (DCM) and stirred for about 1 h at room temperature. After stirring, the mixture was cooled and thionyl chloride was gradually added by dropping funnel at 0 °C. After the adding thionyl chloride within 20 min, reaction mixture was stirred for 12 h at 35 °C. Solvent was evaporated by rotary-evaporator and ACPC was obtained as yellow solid powder. The product was washed with DCM, precipitated in hexane for removing unreacted thionyl chloride and finally dried at room temperature under vacuum for 24 h [52].

### E. Synthesis of Linseed Oil Based Macroinitiator

ACPC in DCM was added drop wise to a mixture of the equivalent amount of PGs in pyridine at 0 °C. The temperature was raised to 35 °C and kept constant while stirring for 80 h. The reaction mixture was then dissolved in diethyl ether and washed with 0.1% aqueous sulphuric acid solution and water, then dried over Na<sub>2</sub>SO<sub>4</sub>. Oil based macroinitiator (OBMI) was characterized by FT-IR and <sup>1</sup>H-NMR spectroscopy.

### F. Synthesis of Styrenated Oil by NMRP-mediated Miniemulsion Polymerization

Miniemulsion was prepared according to the following procedure: 0.2 g (1.5x10<sup>-4</sup> mol) OBMI and 1 g styrene (9.6x10<sup>-3</sup> mol) were mixed with a given amount of HD (4 %, by weight of styrene) and TEMPO (1.5x10<sup>-4</sup> mol) to form organic phase and stirred with magnetic stirrer for 20 min. This mixture was then slowly added to the separately prepared 50 ml aqueous solution of DOWFAX 8390 and stirred for 20 min. The mixture was ultrasonified by using an ultrasonifier (Bandelin SONOPLUS HD 3200, amplitude 70%, 400 W) for a time period of 15 min. The obtained miniemulsion was deoxygenated by purging with

nitrogen for 10 min and transferred to the reactor. The temperature was set to 125 °C and after the required durations, samples were taken from reaction medium. The polymer product was precipitated twice in tenfold methanol and dried at 30 °C under vacuum for 24 h. The polymerization yields were determined gravimetrically. The styrenated oil samples were also prepared by classical NMRP polymerization in solvent (xylene) in order to compare the results with those of the samples of this study under miniemulsion conditions.

### G. Determination of Film Properties

Film properties of styrenated oil samples obtained by miniemulsion were determined. Drying time [53], flexibility [54], adhesion [55], water resistance [56], alkali resistance [56] and acid resistance [56] tests were applied according to standard methods. For each test method, sample was thinned with xylene to 30% solid content, and 0.5% lead naphthenate and 0.05% cobalt naphthenate as metal based on solid content were added. Film coating was applied after 24 h. For drying time test, polymer films (60 μm) were prepared on glass surfaces by using a film applicator. The flexibility, water resistance and adhesion tests were applied by using tin plate panels as a substrate. For alkali and acid resistance tests, dipping method was employed by using glass tubes as explained in the related standards.

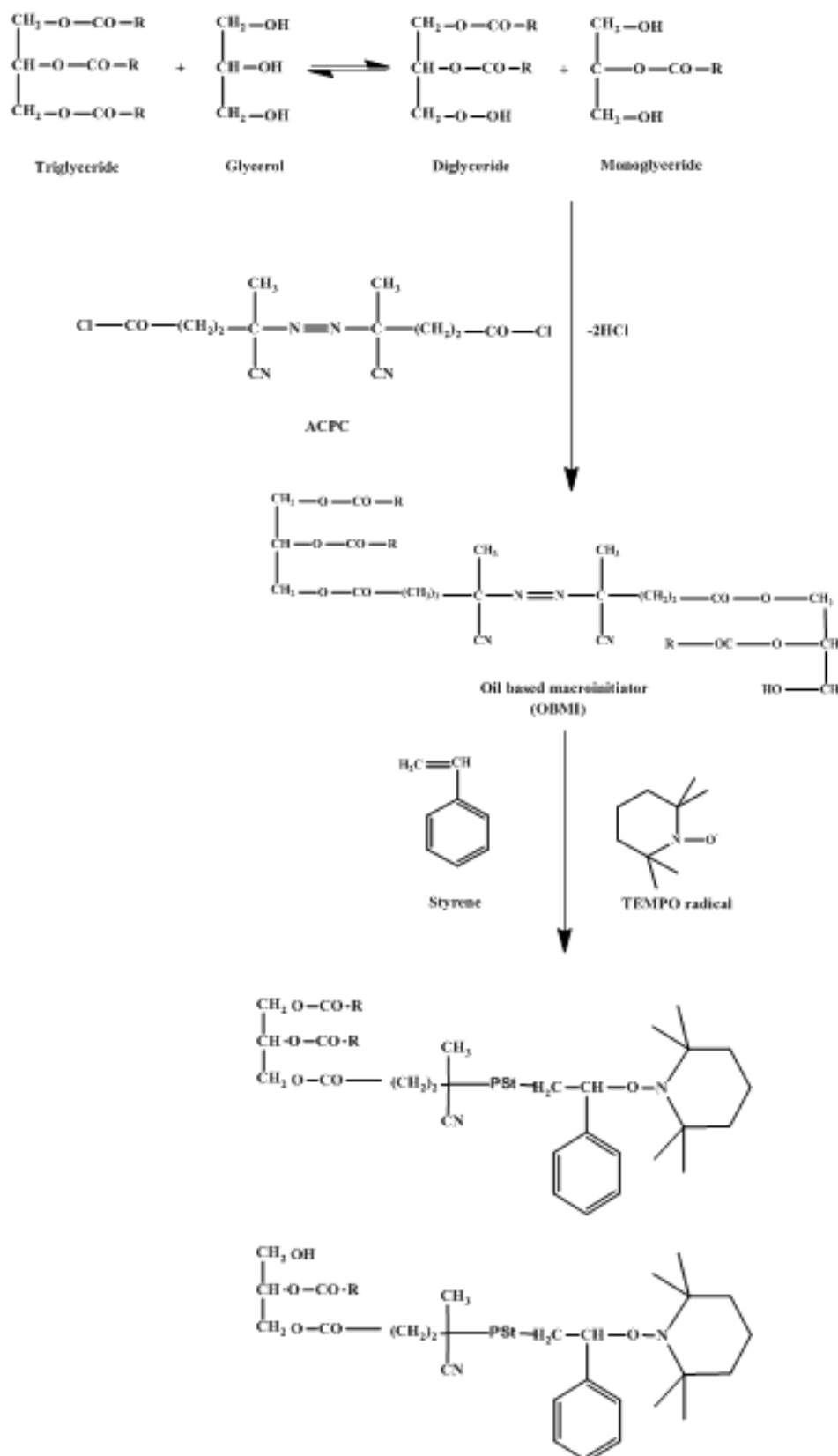
## III. RESULTS AND DISCUSSION

As mentioned before, in this study styrenated oil preparation was realized by NMRP under miniemulsion conditions. It is well known that the application of NMRP under macroemulsion conditions showed the colloidal instability [28, 29]. By taking this fact into account, in the current study this polymerization was carried out by macroinitiator method under miniemulsion conditions. In order to obtain a macroinitiator, linseed oil PGs were prepared and esterified with ACPC in order to insert thermally liable azo groups into the oil-based initiator structure. ACPC was synthesized from ACPA by converting acid groups to acid chlorides by means of thionyl chloride [52]. Since the azo groups of ACPA is thermally liable, in the esterification reaction, acid chloride was used in order to perform the reaction at low temperature to protect azo groups from decomposition. Macroinitiator thus prepared was subjected to polymerization with styrene. The overall process and the representative structure of the styrenated oil sample is explained in Scheme 1.

The hydroxyl and acid values of PGs were found as 116 mg.KOH/g and 5.8 mg.KOH/g, respectively. The hydroxyl value of PGs was in the same level as that of previously used in the preparation of styrenated oil samples which showed good film properties [14].

The FT-IR spectrum of ACPC is given in Fig. 1. FT-IR spectrum of ACPC gave the peak of carbonyl group (-C=O) at 1793 cm<sup>-1</sup>. Characteristic band of (-CN) groups

occurred at  $2240\text{ cm}^{-1}$ . Strong peaks at  $560\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$  carboxyl group of ACPA at  $1700\text{ cm}^{-1}$  was shifted to  $1793\text{ cm}^{-1}$  were attributed to (C-Cl) of ACPC. The peak of  $\text{cm}^{-1}$  and this indicates that the acid chloride was formed.



Scheme 1. Representative styrenated oil structure obtained by NMRP technique



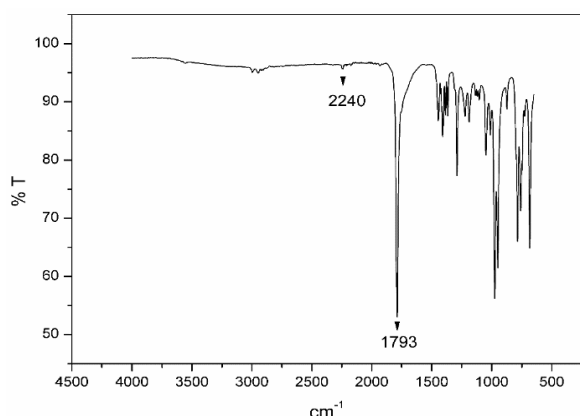


Fig. 1. FT-IR spectrum of ACPC

As seen in Scheme 1, OBMI was prepared by esterification of PGs with ACPC. The macroinitiator structure was examined by FT-IR and <sup>1</sup>H-NMR analysis. FT-IR spectrum of OBMI is given in Figure 2. (C=O) stretching band of oil portion was observed at 1735 cm<sup>-1</sup>. Peaks at 2850-2900 cm<sup>-1</sup> were attributed to C-H bond. Characteristic peak of (-CN) groups occurred at 2244 cm<sup>-1</sup>.

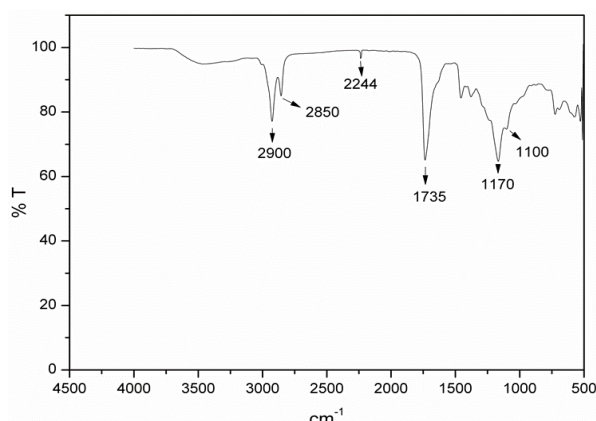


Fig. 2. FT-IR spectrum of OBMI

The <sup>1</sup>H-NMR spectrum of OBMI, as shown in Fig. 3, signals observed at the range of 0.8–0.9 ppm resulted from CH<sub>3</sub> groups. CH<sub>2</sub> protons of oil moiety was seen at the range of 3.5-4.2 ppm. Signals at 2.0-2.4 were attributed to (CH<sub>2</sub>)<sub>2</sub> protons. CH protons of oil moiety were seen at 5.3 ppm [14, 15].

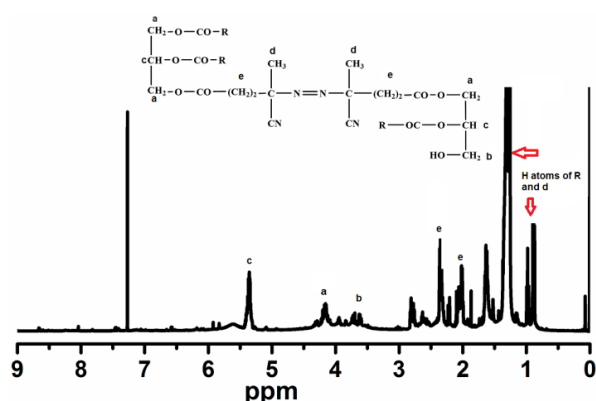


Fig. 3. <sup>1</sup>H-NMR spectrum of oil-based macroazoinitiator

As mentioned before, the styrenation process was carried out by NMRP under miniemulsion conditions. It is well known that NMRP technique has more severe problems regarding colloidal instability in macroemulsion polymerization due to high reaction temperature and long reaction time [28]. At a high temperature the surfactant decomposed and caused colloidal instability [28]. By taking this fact into account, in the present study, styrenation process was realized by NMRP in miniemulsion with a high temperature resistant surfactant, DOWFAX 8390. As a cosurfactant HD was used. In miniemulsion polymerization, contrary to macroemulsion polymerization, droplet nucleation is dominant and polymerization progresses in droplets without monomer diffusion while it is essential for macroemulsion polymerization [28, 38, and 44]. Additionally, in conventional emulsion polymerization with NMRP, degree of water solubility of nitroxide greatly effect the control of polymerization. While very low water solubility of nitroxide results in an uncontrolled polymerization, high water solubility causes slow aqueous phase initiation [28, 34].

In this study, since ingredients are all hydrophobic structure and water insoluble, the polymerization was forced to occur within the droplets and above mentioned drawbacks were avoided in the application of NMRP in miniemulsion system.

Nano-sized polymer particles are obtained in miniemulsion polymerization because, droplets are almost constant in size throughout the reaction. In literature, in order to define the polymerization as miniemulsion polymerization, droplet/particle size at the beginning and/or at the end of the reaction were determined and if the measured size is within the range of miniemulsion, the polymerization was decided as miniemulsion polymerization [45-50]. In the present study, we applied a strategy to determine ideal conditions for miniemulsion polymerization. This strategy was based on measuring the droplet/particle size throughout the polymerization carried out with different amount of surfactant. In this way, the conditions of being 1:1 copy [43, 44] for droplets/particle were more accurately determined.

Droplet/particle sizes were measured by DLS analysis. Droplet/particle diameters and diameter polydispersities (D-PDI) for all samples (SO-TMP1-3) are given in detail in Table 1.

The smallest standard deviation in diameter was obtained in the case of SO-TMP2 sample, and naturally the effective diameter remained practically unchanged during the course of reaction. This showed that monomer diffusion to the polymer particles was prevented to a great extent under the applied conditions. Consequently, polymerization occurred in the monomer droplets initially formed by shearing forces. This behaviour fit the miniemulsion polymerization mechanism [43, 44].

TABLE I  
DROPLET/PARTICLE DIAMETERS AND DLS POLYDISPERSITIES FOR ALL STYRENATED OIL SAMPLES

Sample*	Time (h)	Effective Diameter (nm)	D-PDI	Standard Deviation
SO-TMP1 (DOWFAX 8390: 12 wt. % of monomer)**	0	220.7	0.091	19.18
	6	178.1	0.115	
	12	213.4	0.104	
	24	213.4	0.108	
SO-TMP2 (DOWFAX 8390: 24wt. % of monomer)**	0	195.0	0.111	15
	6	189.2	0.107	
	12	221.5	0.119	
	24	191.2	0.124	
SO-TMP3 (DOWFAX 8390: 48 wt. % of monomer)**	0	128.3	0.116	95.8
	6	128.3	0.143	
	12	155.5	0.103	
	24	327.3	0.098	

\* SO-TMP1-3 are the styrenated oil samples prepared under the explained conditions.

\*\* Surfactant amount in the reaction.

The DLS graphs of SO-TMP1-3 are also given in appendix. The change of droplet/particle size throughout the reaction at all conditions can be easily seen in these graphs.

SO-TMP2 sample which obtained with the determined ideal surfactant concentration was used in the structure determination and characterization studies. FT-IR, <sup>1</sup>H-NMR and GPC analyses were applied. As seen from the FT-IR spectrum in Fig. 4, SO-TMP2 obtained from 24 h reaction showed the characteristic bands of both styrene and ester groups of the oil portion. The peaks at 1600 cm<sup>-1</sup> and 1495 cm<sup>-1</sup> are assigned to aromatic C=C stretching and peak at 1740 cm<sup>-1</sup> is due to ester groups. Thus, FT-IR results showed the attachment of polystyrene segments to the oil moiety.

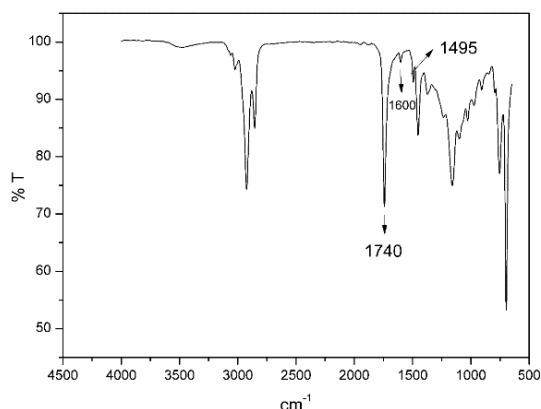


Fig. 4. FT-IR spectrum of SO-TMP2 (24 h)

SO-TMP2 sample was further analysed by <sup>1</sup>H NMR analysis. As seen from Fig. 5, signals observed at the range of 6.4–7.3 ppm are attributed to aromatic protons of styrene. These aromatic protons of phenyl groups in the resulting product showed the attachment of polystyrene

segments to the oil moiety. TEMPO terminated polystyrene exhibited sets of signals at 4.3–4.4 ppm.

TEMPO moieties were observed at 0.2–1.7 ppm. CH<sub>2</sub> and CH<sub>3</sub> groups in the OBMI moiety displayed signals at 0.9–2.3 ppm [14].

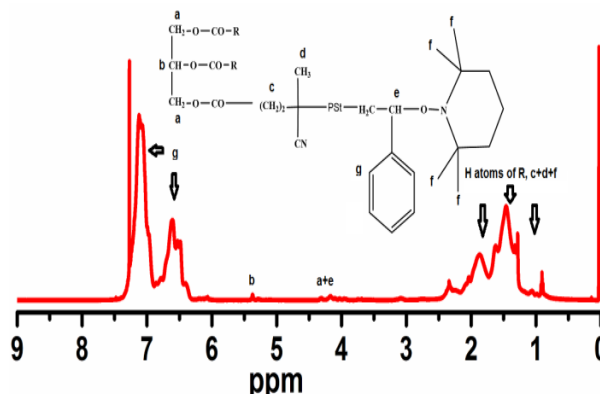


Fig.5. <sup>1</sup>H-NMR spectrum of SO-TMP2 (24 h)

GPC curves of SO-TMP2 at 6, 12 and 24 h reaction times are shown in Fig. 6. As seen, samples showed unimodal curves. This is an expected result because OBMI gives free radicals having molecular mass which are close to each other.

It should be noted that in our unpublished work, styrenated oil samples obtained from air-blown linseed oil showed deviation from unimodality due to the big difference in the molecular mass of free radicals.

Molecular weight, molecular weight distribution and conversions of SO-TMP2 sample at different time intervals throughout the miniemulsion polymerization are given in Table 2.

In order to understand the effect of miniemulsion conditions on the PDI, the results of the samples obtained by NMRP in xylene were also included.

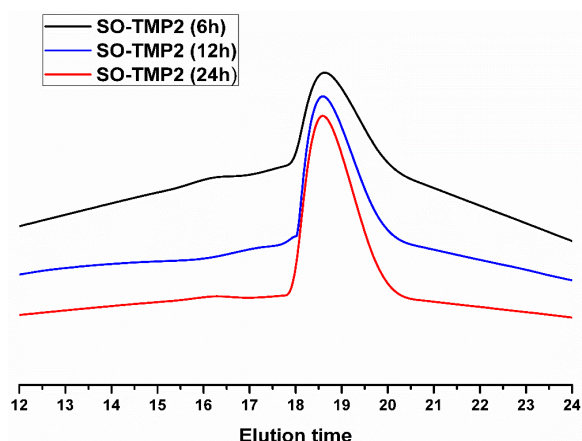


Fig. 6. GPC curves of SO-TMP2 samples

SO-TMP2 (24 h) sample has a lower PDI than that of TMP-SOL sample of 24 h reaction. Additionally, in order to understand the effect of TEMPO amount, miniemulsion polymerization was carried out with OBMI/TEMPO ratio of 1/2 and the resulting sample (SO-TMP2 (1/2)) showed lower molecular weight and PDI as 1.41. This PDI value is close to the results of NMRP carried out with ordinary monomers such as styrene and n-butyl acrylate [32, 33, 57, and 58]. It should be emphasized that although OBMI has a larger molecular weight, a low PDI value could be obtained due to its hydrophobic nature which prevented the monomer diffusion. The another factor, as explained above, is the formation of radicals having molecular weight which were very close to each other.

TABLE II

THE CHANGE OF MOLECULAR WEIGHT AND POLYDISPERSITY OF STYRENATED OIL SAMPLES OBTAINED IN THE PRESENCE OF TEMPO IN DIFFERENT REACTION TIMES IN MINIEMULSION AND SOLUTION POLYMERIZATION CONDITIONS

Sample	t (h)	Mn <sup>a</sup>	Mw <sup>a</sup>	PDI <sup>a</sup>	Conversion <sup>b</sup> (%)
SO-TMP2	6	8465	13919	1.64	24.41
SO-TMP2	12	8829	16448	1.86	31.18
SO-TMP2	24	9330	16589	1.78	39.67
SO-TMP2(1/2)	24	5720	8071	1.41	28.42
TMP-SOL <sup>c</sup>	12	9023	15520	1.72	29.13
TMP-SOL <sup>c</sup>	24	12561	25247	2.01	34.50

<sup>a</sup> Molecular weight estimated by GPC based on thought to be obtained by miniemulsion polymerization. polystyrene standards.

<sup>b</sup> Conversion was determined gravimetrically.

<sup>c</sup> Samples prepared by NMRP in xylene.

Additionally, the conversion and  $\ln[(M_0/M)]$  values are given in Table 3 for SO-TMP1-3 samples. The graphs of  $\ln[(M_0/M)]$  against time were constructed.

As seen in Fig. 7 and a straight line was obtained for each sample indicating that the polymerization has controlled 'living' characteristics for all samples [59-61].

If we consider droplet/particle sizes of 128.3, 327.3 nm only at the beginning and at the end, all samples were

In this case, there would be a conflict about which samples kinetic data should be used in design calculation. As seen in Fig. 7, in the  $[\ln(M_0/M)]$  vs. time graph the best fit was found for SO-TMP2 sample.

Additionally, in Fig. 7 the sample SO-TMP2 (1/2) gave the least slope, as compared to others. This is due to the excess amount of TEMPO which acted retarder [62]. These results were in consistent with those of reached by droplet/particle size change during reaction as explained in Table 1.

TABLE III CONVERSION AND LN  $[(M_0/M)]$  VALUES FOR ALL SO-TMP SAMPLES FOR EACH REACTION TIME

t (h)	SAMPLE			
	SO-TMP1		SO-TMP2	
	Conver. (wt.%)	$\ln[(M_0/M)]$	Conver. (wt.%)	$\ln[(M_0/M)]$
6	21.14	0.24	24.41	0.28
12	27.44	0.32	31.18	0.37
24	32.18	0.39	39.67	0.51
t (h)	SO-TMP3		SO-TMP2 (1/2)	
	Conver. (wt.%)	$\ln[(M_0/M)]$	Conver. (wt.%)	$\ln[(M_0/M)]$
	6	17.56	0.19	15.48
12	26.47	0.31	19.12	0.21
24	34.14	0.42	23.74	0.27

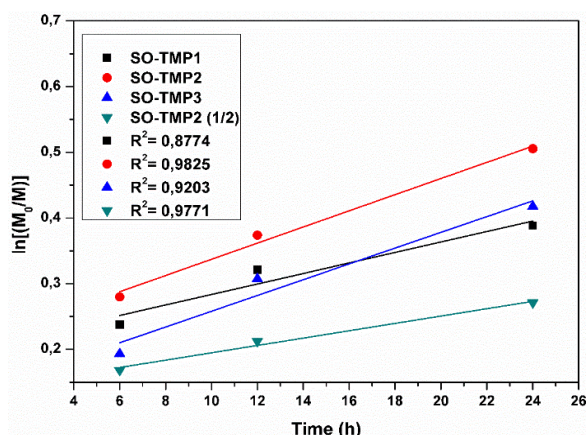


Fig. 7. Time dependence of  $\ln [(M_0/M)]$  for NMRP miniemulsion polymerization in all SO-TMP conditions

For the evaluations of SO-TMP2 sample in view of an oil-based binder, films were tested according to related standard test methods. Film properties and results are summarized in Table 4.

TABLE IV FILM PROPERTIES OF STYENATED OIL SAMPLE (SO-TMP2) PREPARED IN NMRP ADAPTED MINIEMULSION CONDITION

Flexibility <sup>a</sup>	Adhesion <sup>b</sup>	Drying Time <sup>c</sup> (Set to touch)
2 mm	4B	3 min
Alkali Resistance <sup>d</sup>	Acid and Water Resistance <sup>e</sup>	
44 min	No Change	

The samples prepared by NMRP technique in miniemulsion condition showed good flexibility, drying time and water/acid resistances.

a The smallest diameter of cylinder which caused no crack on the film [54].

b Test method B was applied [55].

c The test was carried out at 25 °C and 60% relative humidity [53].

d Time for first appearance of peeling. Test was carried out at 25 °C with 5% NaOH solution [56].

e Test was carried out at 25 °C with 9% H<sub>2</sub>SO<sub>4</sub> solution [56].

e Time for the disappearance of whiteness for water resistance [56].

As a result, in the present study, oil-based macroazoinitiator of linseed oil PGs successfully incorporated into the oil-styrene copolymer structure with NMRP under determined ideal miniemulsion conditions. Oil-styrene copolymer thus obtained showed low PDI and good film properties as a coating material.

#### IV.CONCLUSION

In this study, it was aimed to obtain styrenated oil as a coating material by NMRP technique in miniemulsion

conditions. Ideal surfactant concentration was experimentally determined by using a new strategy based on the measuring of droplet/particle size through the polymerization. In this way, ideal surfactant concentration, which prevents the monomer diffusion, was determined and used in polymerization. The polymerization was also carried out in xylene for determining the effect of miniemulsion conditions on PDI. PDI values of SO-TMP2 sample were found to be 1.86 and 1.78 for 12 and 24 h reactions, respectively, for the polymerization carried out in miniemulsion medium.

As seen, PDI values in the miniemulsion polymerization was found to be close to those of samples obtained in xylene. Droplet/particles were 1:1 copy of the initial droplets during the miniemulsion polymerization. In ideal miniemulsion condition experimentally determined, complex nucleation mechanism of macroemulsion were avoided and the reaction was occurred in the droplets called as ‘nanoreactors’. Finally, film properties of SO-TMP2 were evaluated according to related standard test methods. Test results showed that SO-TMP2 sample could be used as an oil-based binder with good flexibility, drying time and acid/water resistances.

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#### REFERENCES

- [1] Swern, D., Bailey's Industrial Oil and Fat Products, 3rd ed., John Wiley & Sons, New York, 1964.
- [2] Payne, H.F., Organic Coating Technology (Oils, Resins, Varnishes and Polymers), Polytechnic Institute of Brooklyn, 1954.
- [3] Panda, H., Alkyd Resins Technology Handbook, Asia Pacific Business Press Inc., 2010.
- [4] Board, N., Modern Technology Of Oils, Fats & Its Derivatives, National Institute of Industrial Research, Asia Pasific Business Press Inc., India, 2002.
- [5] Erkal, F.S., Erciyes, A.T., Yagci, Y. (1993) J. Coatings Technol. 65, 37–43.
- [6] Kabasakal, O.S., Güner, F.S., Arslan, A., Ergan, A., Erciyes, A.T., Yagci, Y. (1996) J. Coatings Technol. 68, 57–62.
- [7] Kabasakal, O.S., Güner, F.S., Erciyes, A.T., Yagci, Y. (1995) J. Coatings Technol. 67, 47–51.
- [8] Güner, F.S., Erciyes, A.T., Kabasakal, O.S., Yagci, Y. (1998) Transworld Res. Network, Trivandrum 2, 31–51.
- [9] Güner, F.S., Yagci, Y., Erciyes, A.T. (2006) Prog. Polym. Sci. 31, 633–670.
- [10] Erkal, F.S., Usta, S., Erciyes, A.T., Yagci, Y. (2000) J. Coatings Technol. 72, 107–110.
- [11] Gultekin, M., Beker, U., Erkal, F.S., Erciyes, A.T., Yagci, Y. (2000) Macromol. Mater. Eng. 283, 15–20.
- [12] Akbas, T., Beker, U.G., Güner, F.S., Erciyes, A.T., Yagci, Y. (2003) J. Appl. Polym. Sci. 88 (10), 2373–2376.
- [13] Alemdar, N., Erciyes, A.T., Yagci, Y. (2010) Prog. Org. Coat. 67, 55–59.
- [14] Alemdar, N., Erciyes, A.T., Yagci, Y. (2009) Prog. Org. Coat. 66 (2), 99–106.
- [15] Alemdar, N., Erciyes, A.T., Bicak, N. (2012) J. App. Pol. Sci. 125 (1), 10-18.
- [16] Alemdar, N., Erciyes, A.T., Bicak, N. (2010) Prog. Org. Coat. 69, 522-526.



[17] Sugino, Y., Yamamoto, K., Miwa, Y., Sakaguchi, M. and Shimada, S. (2003) *epolymers* 7, 1-8.

[18] Zhuang, Y., Zhao, X. and Zhang, M. (2008) *Polymer* 49, 3457-3461.

[19] Lopez, R.G., D'Agosto F. and Boisson, C. (2007) *Prog. Polym. Sci.* 32, 419-454.

[20] Liu, X., Zhang, G., Li, B., Bai, Y., Pan, D. and Li, Y. (2008) *European Polymer Journal* 44, 1200-1208.

[21] Veregin R.P.N., Odell P.G., Michalak L. M. and Georges, M.K. (1996) *Macromolecules* 29,2746-2754.

[22] Scotta, A.J., Nabifara, A., Hernández-Ortizb, J.C., McManusa, N.T., Vivaldo-Limab, E., Penlidis, A. (2014) *European Polymer Journal* 51, 87-111.

[23] Fukuda, T., Terauchi, T., Goto, A., Ohno, K., Tsujii, Y., Miyamoto, T., Kobatake, S., Yamada, B. (1996) *Macromolecules* 29, 6393.

[24] Jaymand, M. (2011) *Polymer* 52, 21, 4760-4769.

[25] Li, J., Zhu, X., Zhu, J., Cheng, Z. (2007) *Radiation Physics and Chemistry* 76, 1, 23-26.

[26] Lia, F., Zhanga, L., Chena, Y. (2010) *Optical Materials* 34, 9, 1563-1569.

[27] Zhao, B. (2003) *Polymer* 44, 15, 4079-4083.

[28] Cunningham M. F. (2003) *Chimie* 6, 1351-1374.

[29] Nicolas, J., Charleux, B., Guerret, O., Magnet, S. (2004) *Angewandte Chemie International Edition* 43, 6186-6189.

[30] Marestin, C., Noël, C., Guyot, A., Claverie, J. (1998) *Macromolecules* 31, 4041.

[31] Cunningham M. F. (2003) *Chimie* 6, 1351-1374.

[32] Pan, G., Sudol, E.D., Dimonie, V.L., El-Aasser, M.S. (2001) *Macromolecules* 34, 481.

[33] Pan, G., Sudol, E.D., Dimonie, V.L., El-Aasser, M.S. (2002) *Macromolecules* 35, 6915.

[34] Nicolasa, J., Guillaneuf, Y., Lefay, C., Bertin, D., Gignes, D., Charleux, B. (2013) *Progress in Polymer Science* 38, 63-235.

[35] Lansalot, M., Charleux, B., Vairon, J.-P., Pirri R., Tordo, P. (1999) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 40 (2), 317.

[36] Cao, J., He, J., Li, C., Yang, Y. (2001) *Polym. J.* 33, 75.

[37] Bon, S.A.F., Bosveld, M., Klumperman, B., German, A.L. (1997) *Macromolecules* 30, 324.

[38] Heiskanen, N., Jamsa, S., Paajanen, L., Koskimies, S. (2010) *Prog. Org. Coat.* 67, 329-338.

[39] Van Hamersveld, E.M.S., Van Es, J.J.G.S., German, A.L., Cuperus, F.P., Weissenborn, P., Hellgren, A.C. (1999) *Prog. Org. Coat.* 35, 235-246.

[40] Guo, J., Schork, J.F. (2008) *Macromol. React. Eng.* 2, 265-276.

[41] Wang, S.T., Schork, J.F., Poehlein, G.W., Gooch, J.W. (1996) *Journal of Applied Polymer Science*, 60, 2069-2076.

[42] Uschanova, P., Heiskanen, N., Mononen, P., Maunua, S.L., Koskimies, S. (2008) *Progress in Organic Coatings*, 63, 92-99.

[43] Cunningham, M.F. (2002) *Prog. Polym. Sci.* 27, 1039-1067.

[44] Mittal, V., *Miniemulsion Polymerization Technology*, BASF SE, Polymer Research, Germany, 2010.

[45] Yang, L., Luo, Y., Li, B. (2006) *Polymer* 47, 751-762.

[46] Zhou, X., Ni, P., Yu, Z. (2007) *Polymer* 48, 6262-6271.

[47] Liu, S., Hermanson, K. D., Kaler, E. W. (2006) *Macromolecules* 39, 4345-4350.

[48] Chakrabarty, A., Singha, N.K. (2013) *J. Colloid Interface Sci.* 408, 66-74.

[49] Boursier, T., Chaduc, I., Rieger, J., D'Agosto, F., Lansalot M., Charleux, B. (2011) *Polym. Chem.* 2, 355-362.

[50] Smulders, W. W., Jones, C. W., Schork F.J. (2005) *AIChE Journal* 51, 3, 1009-1021.

[51] Cocks, L.V., Rede, C.V., *Laboratory Handbook for Oil and Fat Analysts*, Academic Press, London/New York, 1966.

[52] Yagci, Y. (1985) *Polymer Communications* 26, 7-8.

[53] ASTM D 1640-03, Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature, Annual Book of ASTM Standards, vol. 06.01, pp. 1-3.

[54] DIN 53152, Deutsche Normen, Deutscher Normenausschuss (DNA), October 1959.

[55] ASTM D 3359-90, Standard Test Methods for Measuring Adhesion by Tape Test, Test Method B, Annual Book of ASTM Standards, vol. 06.01, 1991, pp. 511-514.

[56] ASTM D 1647-89, Standard Test Methods for Resistance of Dried Films Varnishes to Water and Alkali, Annual Book of ASTM Standards, vol. 06.01, 1991, pp. 236-237.

[57] Prodpran, T., Dimonie, V.L., Sudol, E.D., El Aasser, M.S. (2000) *Macromolecular Symposia* 155, 1.

[58] MacLeod, P.J., Barber, R., Odell, P.G., Keoshkerian, B., Georges, M.K. (2000) *Macromolecular Symposia* 155, 31.

[59] Fischer, A., Brembilla, A., Lochon, P. (2001) *European Polymer Journal* 37, 33-37.

[60] Zetturland, P. B., Saka, Y., Mchale, R., Nakamura, T., Aldabbagh, F., Okubo, M. (2006) *Polymer* 47, 7900-7908.

[61] Hong, J., Wang, Q., Lin, Y., Fan, Z. (2005) *Macromolecules* 38, 2691-2695.

[62] Zhang, X., Giani, O., Monge, S., Robin, J.J. (2010) *Polymer* 51, 2947-2953.

APPENDIX

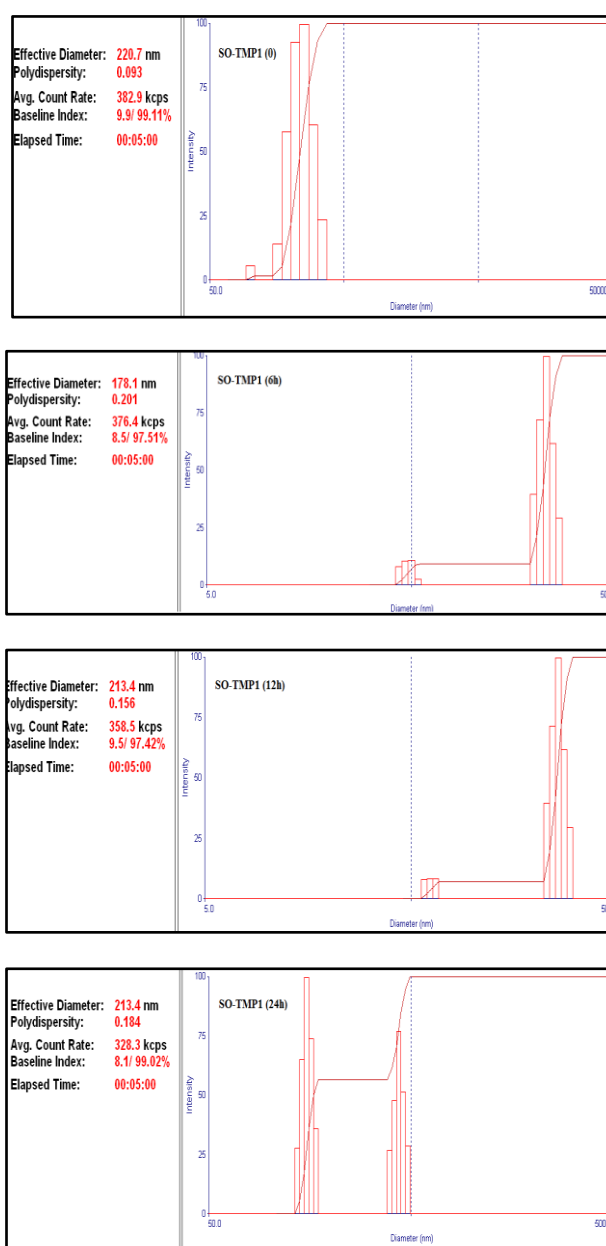


Fig. 8. DLS graphs for SO-TMP1 samples

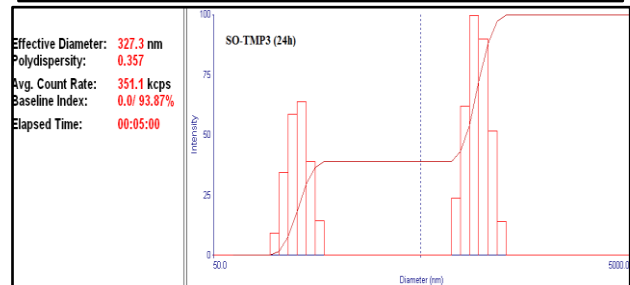
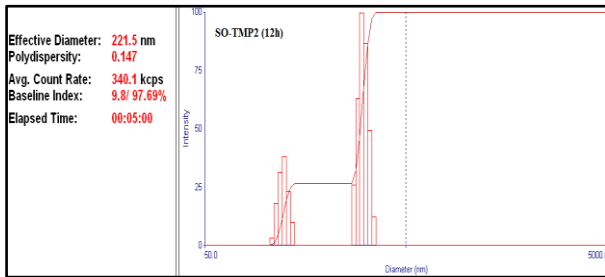
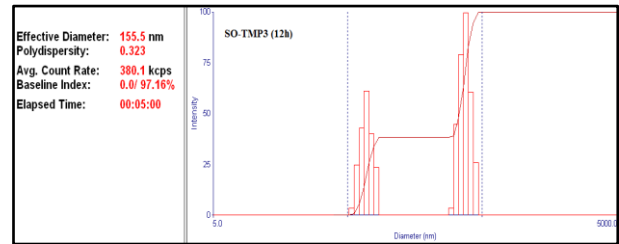
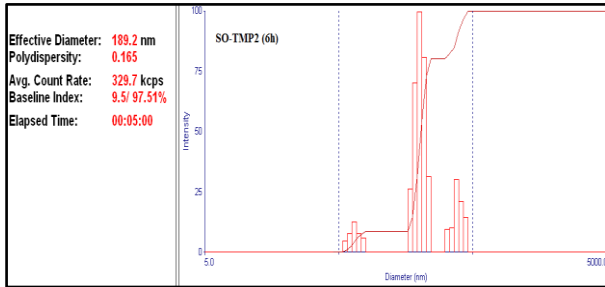
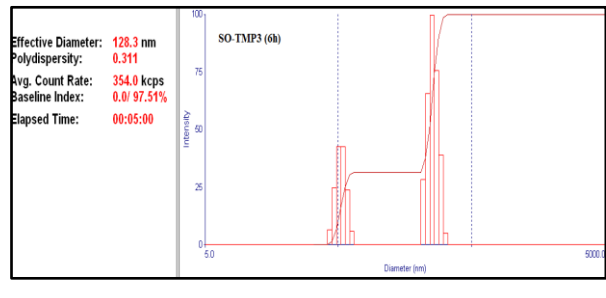
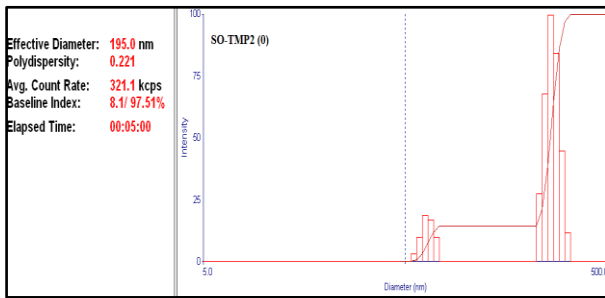


Fig. 10. DLS graphs for SO-TMP3 samples

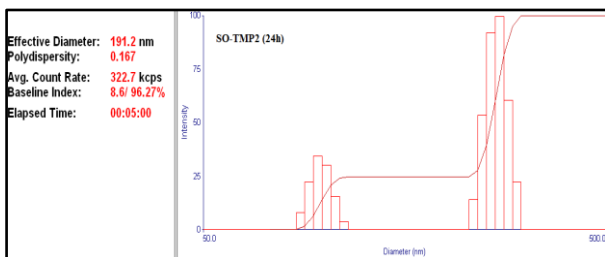


Fig. 9. DLS graphs for SO-TMP2 samples

