

Styrenated Sunflower Oil Polymers from Raft Process for Coating Application

Neslihan Alemdar,¹ A. Tuncer Erciyes,¹ Niyazi Bicak²

¹Department of Chemical Engineering, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

²Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

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ABSTRACT: Oil-based macroinitiator (MI) obtained from sunflower oil was styrenated using reversible addition–fragmentation chain transfer polymerization (RAFT) in the presence of phenacyl morpholine dithiocarbamate (PMDC) as chain transfer agent. The solvent effect and effect of the molar ratio of the transfer agent, PMDC, on polydispersity and molecular weight of the polymers were investigated. The obtained results showed that, 1,4-dioxane is a better solvent and 1/4 molar ratio of [MI]/[PMDC] provides relatively low polydispersities. No homopolystyrene was detected under these conditions, indicating the efficiency of PMDC in the chain transfer process. Livingness

of the polymerization process was confirmed by chain extension with styrene using the preformed polymer as macrotransfer agent. The film properties of styrenated oil samples were determined according to the related standards. To improve film properties, the polymer obtained by RAFT technique was modified by reaction with MI. The resulting material gave transparent films with good film properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 10–18, 2012

Key words: triglyceride oil; coatings; controlled/living polymerization; RAFT

INTRODUCTION

Controlled/living radical polymerization (CLRP) methods have found extensive use for creating various macromolecular architectures of the past decade. Among these methods, reversible addition–fragmentation chain transfer polymerization (RAFT)^{1–4} technique is of special importance because it is tolerant of a wide range of functionality in the monomer and solvent.⁵ In the RAFT process, the control of chain growth depends largely on the structure of the monomer and transfer agent. In this technique, dithioesters or trithiocarbonates are generally employed as the chain transfer agent and the free radicals forms an intermediate with these agents, which in turn undergoes fragmentation yielding a new radical to grow. Some of these growing chains are combined with each other and termination occurs.

In the present work, RAFT technique was employed in controlled styrenation of oils for coating applications. Since it imparts good film properties to oil, styrenation of oil is one of the traditional arts in coating industry. However, in the classical styrenation method, homopolystyrene formation occurs and it causes the film to be opaque which is

the main drawback of the current processes. The methods by which homopolymerization can be minimized and polymer structure can be controlled, were previously developed in our laboratory.^{6–11} In our very recent studies, the styrenated oil with controlled structure and narrow polydispersity was obtained by using nitroxide-mediated radical polymerization (NMRP) method as one of the CLRP techniques.^{12,13}

As a continuation of these studies, in the present work, we aimed at preparing styrenated oil by RAFT technique. Comparing with NMRP, this technique operates at lower temperatures (i.e., 60–90°C). Consequently, other transfer reactions are minimized. This advantage makes it preferable to NMRP. Taking this advantage, we have decided to styrenate the sunflower oil using RAFT methodology. For this purpose, an oil-based macroinitiator (MI) having thermally labile azo groups was prepared from sunflower oil, and this MI was then employed in polymerization of styrene by using phenacyl morpholine dithiocarbamate (PMDC) as RAFT agent. PMDC was chosen as transfer agent due to its easy leaving phenacyl group. This behavior was considered as beneficial to convert, at earlier stage of the polymerization, all the primary radicals into phenacyl radicals. The effects of various parameters, such as the solvent effect and the amount of PMDC were investigated. Although the obtained polymer had a narrow polydispersity, their film

Correspondence to: A. T. Erciyes (erciyes@itu.edu.tr).

properties showed a deficiency in their flexibility and adhesion properties. To improve these properties, the obtained polymer was further reacted with MI. In this way, flexibility and adhesion were improved due to the fact that an additional soft oil moiety was inserted to structure.

EXPERIMENTAL

Materials

Commercially purchased sunflower oil was used as the oil component. Styrene (St, 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor. Other solvents purified by conventional procedures. 4,4'-Azobis (4-cyanopentanoic acid) (ACPA), analytical grade from Fluka, was used as received. The corresponding acid chloride (ACPC) was obtained by reacting ACPA with phosphorus pentachloride in dry benzene as described in the literature.¹⁴ Carbon disulfide (99.5%, Merck) was used as received. Morpholine (99%, Merck) was stored over sodium metal under nitrogen atmosphere for 24 h and distilled before use.

Characterization

Molecular weights and polydispersities of the polymers were estimated by gel permeation chromatography (GPC) using an Agilent 1100 instrument equipped with a differential refractometer. Tetrahydrofuran (THF) was used as eluent at a flow rate of 0.3 mL min⁻¹. Molecular weights were determined using polystyrene standards.

The structures of products were characterized by using Fourier-transform infrared spectroscopy (recorded on a Perkin-Elmer FTIR Spectrum One B spectrometer).

¹H-NMR and ¹³C-NMR spectra of the products were recorded on a Bruker AC250 (250.133 MHz) nuclear magnetic resonance (NMR) instrument using CDCl₃ as a solvent and as the internal standard.

Preparation of the partial glycerides

The partial glycerides were prepared by the procedure described in the literature.¹⁵ The procedure was performed as follows; sunflower oil (120 g) and glycerol (10.4 g) were placed in the reaction flask and heated to 218°C. Then, 1.2 g Ca(OH)₂ (0.1% of the oil portion) was added to the mixture as a catalyst. The temperature was then increased to 230°C. The transesterification reaction was monitored by aliquot (1–2 mL) taken at predetermined time intervals and these were mixed with 7 mL ethanol. The reaction was ceased when the alcohol solution became clear. The reaction was continued for another 1 h at this temperature. The reaction mixture

was cooled and 200 mL diethyl ether was added. To remove the catalyst and free glycerol, the ethereal solution was washed with sulfuric acid solution (5%) and then with distilled water until the washing became neutral.

The washed ethereal solution dried over sodium sulfate, and the solvent was removed. The hydroxyl content and the acid value of the glyceride product were determined by the methods given in the literature.¹⁶

Synthesis of the oil-based macroinitiator

A certain amount of ACPC in dichloromethane was added drop wise to a mixture of the equivalent amount of partial glycerides in pyridine at 0°C. After 30 min, 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 sulfuric acid solution and water and finally dried over Na₂SO₄. The solvent was removed and the resulting viscous liquid was characterized by FTIR and ¹H-NMR spectroscopy.

Synthesis of phenacyl morpholine dithiocarbamate

This compound was prepared in 68.8% yield, according to the method as described before.¹⁷ m.p.: 129.5°C. UV (CH₂Cl₂): λ_{max}: 300 nm (ε: 4882 mol⁻¹ L cm⁻¹);

FTIR (ATR): 3055, 2920, 2830, 1702, 1470, 1390, 1310, 1280, 1140, 1065, 860, 820, 790, 690, cm⁻¹.

¹H-NMR (250 MHz, CDCl₃, ppm): 7.8 aromatic; 5.0 C—CH₂—S; 3.8–4.4 CH₂.

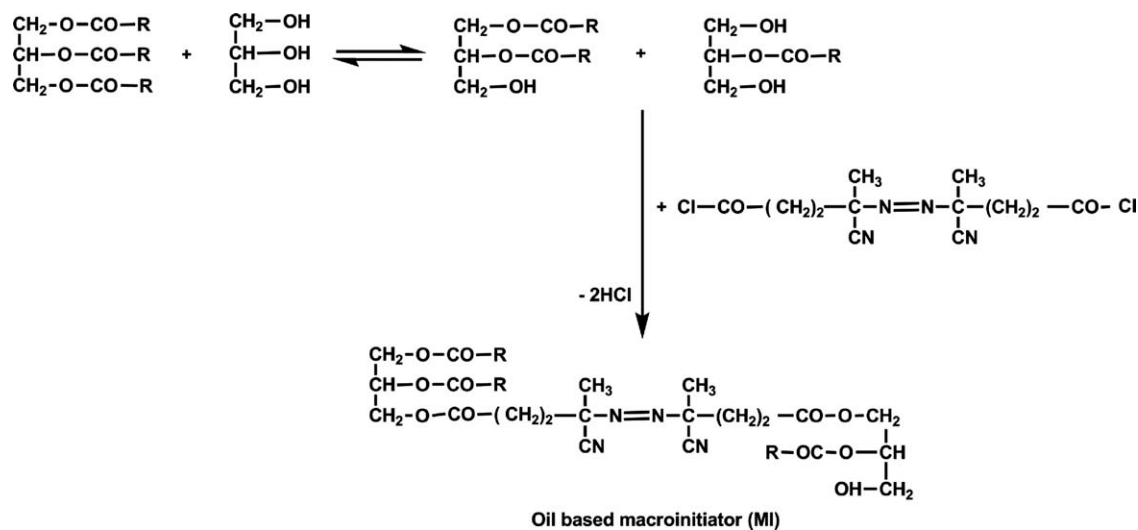
¹³C-NMR (62.5 MHz, CDCl₃, ppm): 44.8, 46.9, 47.3, 50.1, 51.3, 66.2 CH₂; 128.5, 128.7, 133.5, 136.1 aromatic; 193.0 C=O; 195.9 C=S.

Synthesis of styrenated oil by RAFT technique

A given amount of PMDC as a RAFT agent (in varied equivalents with respect to the initiator concentration) was dissolved in 1,4-dioxane or xylene and then added to the flask containing MI (2 g, 1.5 × 10⁻³ mol) and styrene (10 g, 9.6 × 10⁻² mol). The mixture was then purged with nitrogen for 10 min to eliminate oxygen. The vessel was then immersed in an oil bath preheated to 90°C. After the required duration, the reaction was quenched by cooling the flask. The polymer product was precipitated in methanol, filtered, washed with methanol, dried under vacuum at 30°C for 24 h. The polymerizations yields were estimated gravimetrically.

Chain-extension reaction with styrene

A sample of the styrenated polymer (1.4 g, 1.35 × 10⁻⁴ mol) was dissolved in 1,4-dioxane. Then



Scheme 1 Overall process for the synthesis of the MI.

styrene (10 g, 9.6×10^{-2} mol) was added to the mixture and this mixture purged with nitrogen for 10 min. The reaction was continued for another 48 h at 90°C . At the end of this period, the polymer was purified in the same manner as described above. Conversion of styrene was determined gravimetrically.

Reaction of the styrenated oil with oil-based macroinitiator

To improve film properties especially adhesion and flexibility, the styrenated oil was further reacted with the MI to increase oil content of the polymer. For this purpose, the selected styrenated polymer sample (5.6 g, 8.9×10^{-4} mol) was dissolved in 1,4-dioxane. Then, the MI (3.15 g, 2.4×10^{-3} mol) was added to this mixture. The reaction was conducted at 90°C for 48 h under nitrogen atmosphere. Molecular weight and polydispersity of the resulting polymer were estimated by GPC.

Preparation of styrenated oil sample by the classical method

For comparison, the styrenated oil was also prepared by classical styrenation process according to the procedure given in literature.¹⁸ Thus, sunflower oil (11 g, 8.8×10^{-3} mol), styrene (9.0 g, 8.6×10^{-2} mol), xylene (4.6 g, 4.3×10^{-2} mol), and benzoyl peroxide (0.12 g, 4.96×10^{-4} mol) were heated to 150°C for 24 h in an inert medium. At the end of this time, the polymer sample was precipitated in methanol and washed several times with methanol. Then, it was dried in the vacuum. Molecular weight and polydispersity of this polymer were estimated by GPC.

Preparation and characterization of the films

The styrenated oil sample was dissolved in xylene, so that the solid content was to be 70%. The driers, lead naphthenate (0.5% w/w) and cobalt naphthenate (0.05% w/w) were added 24 h before the film application. The resulting viscous solution was employed in the preparation of films. The film properties such as drying time,¹⁹ flexibility,²⁰ adhesion,²¹ hardness,²² water resistance,²³ alkali resistance,²³ and acid resistance²³ were determined. For drying time, hardness and adhesion tests, films of polymers (40 μm) were prepared on glass plate by using an automatic film applicator. In the flexibility, water resistance tests, tin plate panels were used as a substrate. For the other tests (alkali and acid resistance), a dipping method was employed and glass tubes were used as explained in the related standard methods.

RESULTS AND DISCUSSION

In the present study, it was aimed to produce an oil-based surface coating material having better performance, using RAFT polymerization technique. This controlled/living polymerization technique was employed to carry out styrenation of sunflower oil in a controlled manner to avoid formation of homopolystyrene. To introduce polystyrene segments into oil structure, partial glycerides mixture (PGs) were chosen as starting material and used in the synthesis of MI. PGs were obtained by the well known glycerolysis reaction of the sunflower oil. The hydroxyl and acid values of the partial glycerides mixture were found to be 122 mg KOH/g and 2.36 mg KOH/g, respectively.¹⁶ The resulting PGs were esterified with ACPC to produce the MI. The

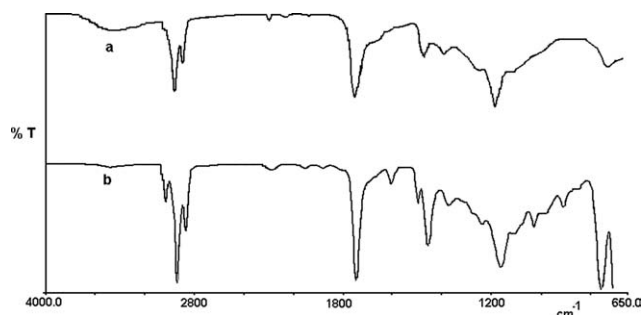


Figure 1 FTIR spectra of MI (a) and styrenated oil sample obtained in the presence of PMDC at 90°C in 1,4-dioxane (b).

glycerolysis reaction and synthesis of the MI is depicted in Scheme 1.

GPC traces of the MI revealed a molecular weight of 1310 g mol⁻¹. The MI was characterized by FTIR and ¹H-NMR spectroscopy techniques [Figs. 1(a) and 2]. The FTIR spectrum of MI gives the peak of the carbonyl group at 1750 cm⁻¹. In the ¹H-NMR spectrum of MI, signals observed at the 0.8–2.5 ppm result from CH₂ and CH₃ groups. The methylene group bearing OH group in MI exhibits signal at around 4.7 ppm.

The prepared MI was employed in RAFT polymerization of styrene in the presence of PMDC as

transfer agent. Although dithiocarbamates are known less efficient in control of styrene or acrylic polymerizations, the electron withdrawing phenacyl group of PMDC was considered to be an easy leaving group to provide quick radical transfer at earlier stages of the polymerization. The electron-rich morpholine group was expected to increase polarity of the chain ends, which makes it less susceptible to radical attack and may induce a negative effect on the control of chain-growth.¹⁷ However, the effect of oxygen in the morpholine ring has not been reported so far. Electron richness of this group, on the other hand, is supposed to reduce the lifetime of the intermediate radical in the RAFT process.

The overall polymerization mechanism is presented in Scheme 2. The polymerization of styrene in 1,4-dioxane using the MI and PMDC as RAFT agent at 90°C for 12 h resulted in styrenated oil with a molecular weight of 6230 g mol⁻¹. In this process, the styrenation temperature was chosen as 90°C which is around the decomposition temperature with 1 h half-life of the oil-based MI.

The structure of the resulting styrenated oil was characterized by means of FTIR and ¹H-NMR spectroscopies [Figs. 1(b) and 2]. FTIR spectrum of the sample shows the characteristic bands of both styrene and initial oil segment. In this spectrum, the

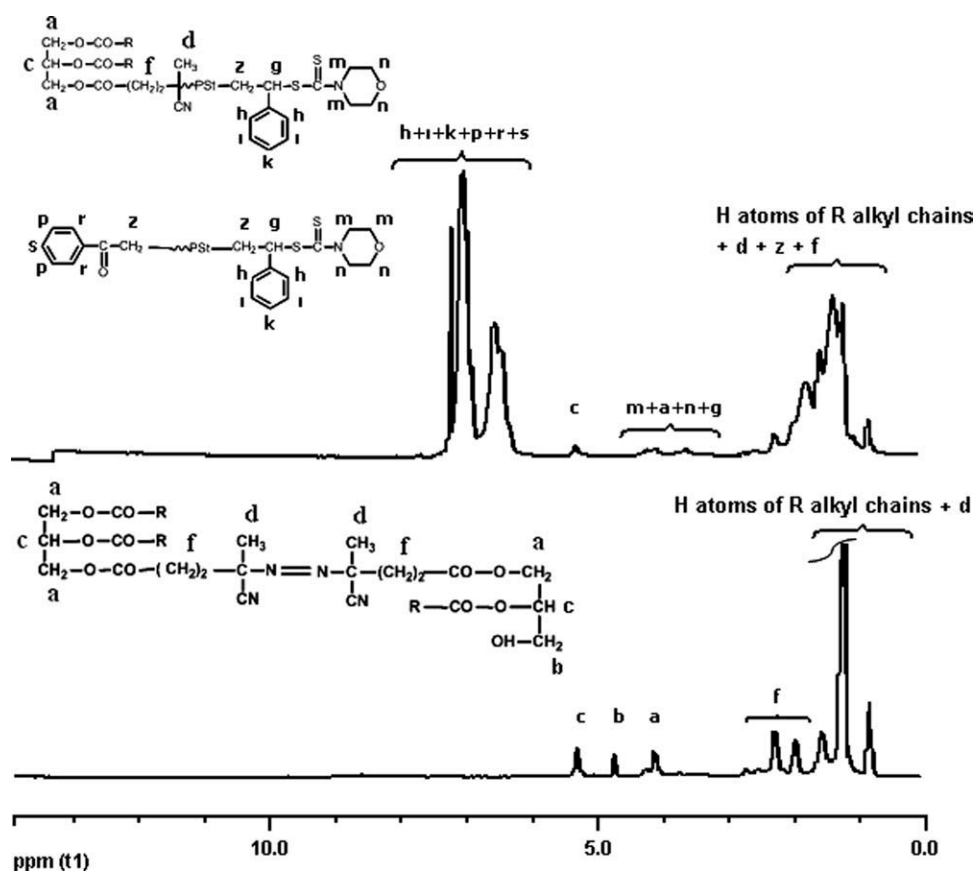
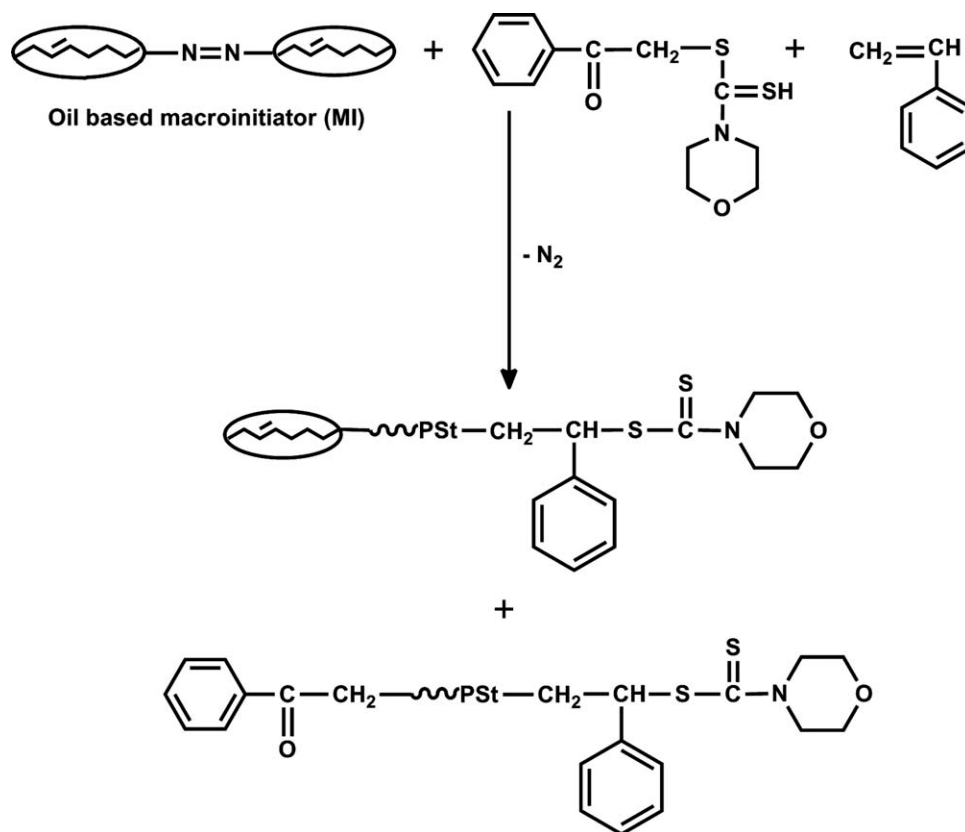


Figure 2 ¹H-NMR spectra of MI and styrenated oil sample by RAFT polymerization in the presence of PMDC in CDCl₃.



Scheme 2 The mechanism of RAFT polymerization of MI and styrene in the presence of PMDC.

carbonyl stretching vibration band appears at 1750 cm^{-1} , skeletal vibration of the phenyl rings of polystyrene segments gives a discernible peak around 1600 cm^{-1} . Moreover, the intense peak emerged at 3080 cm^{-1} might be due to C–H stretching vibration of the phenyl rings of polystyrene segments in the polymer structure.

The $^1\text{H-NMR}$ spectrum of the product, as shown in Figure 3, displays signals at 6.3–7.4 ppm, which can be attributed to aromatic protons of the phenyl rings in the resulting polymer.

To investigate the effect of the PMDC amount, a series of polymerizations was carried out using various $[\text{MI}]/[\text{PMDC}]$ ratios under the same conditions. The molecular weights and polydispersities of the resulting polymers obtained by GPC are tabulated in Table I.

Comparison of the results reveals that, when the amount of PMDC is increased by a factor of two or three the process gives polymers with lower polydispersities (1.46–1.49). The higher $[\text{RAFT agent}]/[\text{initiator}]$ ratio has been demonstrated to ensure good controllability over the molecular weight through addition–fragmentation reactions.²⁴ It should be noticed that in the absence of PMDC, the polymerization yielded a polymer with a polydispersity of 2.01. This polydispersity value is significantly higher

than that of the polymer obtained in the presence of PMDC.

As explained in Table I, the polydispersity reached in RAFT polymerization is 1.46 when the RAFT agent is used two times of the equivalent amount to the free radicals. On the other hand, in

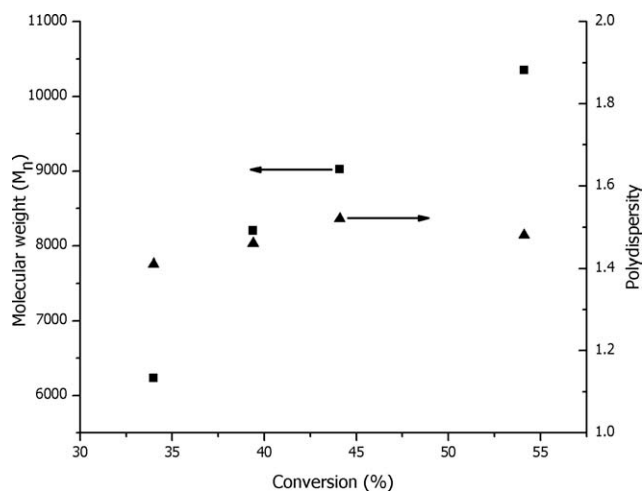


Figure 3 Number of average molecular weight (M_n) versus conversion (■) and polydispersity versus conversion (▲) plots for the RAFT polymerization of styrene with $[\text{MI}]/[\text{PMDC}]: [1/4]$ in 1,4-dioxane at 90°C .

TABLE I
Styrenation of Oil Based Macroinitiator by Varying the Amount of PMDC in 1,4-Dioxane for 24 h at 90°C and in the Absence of PMDC

Sample code	Oil based macroinitiator/PMDC ^a	Conversion ^b (%)	Molecular weight ^c (M_n)	Polydispersity (PDI)
SO	–	60.2	17360	2.01
SO-RAFT1	1/2	44.66	12400	1.69
SO-RAFT2	1/4	39.49	8200	1.46
SO-RAFT3	1/6	38.56	6940	1.49

^a Mol ratio.

^b Conversion of styrene was determined gravimetrically.

^c Estimated by GPC based on polystyrene standards.

the NMRP technique carried out very recently in our laboratory, same level of polydispersity was obtained by using the equivalent amount of 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO) to the free radicals.¹² In both polymerization processes, activated radicals combine with each other to form dead polymer chains. The above explained results show that the frequency of the combination of growing chains is lower in NMRP technique compared to the case of RAFT technique for the system concentrated in this study.

To verify the controlling nature of the process, the kinetics of polymerization was investigated by using the data obtained from the samples taking at appropriate time intervals. The conversions were assigned by gravimetric method and molecular weight and polydispersity data were obtained from GPC. The results are tabulated in Table II and Figure 3. The molecular weight-conversion data represents a nearly linear relationship as shown in Figure 3. This can be ascribed to a nearly constant radical concentration in the polymerization medium. Furthermore, the polydispersities remain around 1.5 throughout the polymerization indicating living/controlled polymerization characteristics.

GPC traces of the polymer samples (Fig. 4) show progressive molecular weight increments with time. The GPC curves of the samples prepared in

the 1,4-dioxane medium are unimodal indicating formation of polymers with closer chain lengths in the process. This result can be ascribed to a good control of the chain growth by PMDC.

To investigate the solvent effect, xylene was also employed as a reaction medium. In these experiments, three-fold excess of xylene was used in comparison to amount of 1,4-dioxane due to lower solubility of PMDC in xylene. In these polymerization, polydispersities of samples were found to be in the range of (1.44–1.56), being in the same range as that found in 1,4-dioxane. However, the conversion attained was around 55% for 300 h, showing that the polymerization in xylene was slower in comparison to that in 1,4-dioxane as shown in Table III and Figure 5.

Comparing the conversions and polydispersities, it is concluded that 1,4-dioxane is better solvent for this process due to higher solubility of PMDC in this solvent. The polymerization kinetics in both solvents gives nearly linear semilog plots (Fig. 6), which can be ascribed to the first order kinetics which implies constant radical concentrations. From the slopes of the curves, the rate constants were found to be

TABLE II
Conversion-Time Data and Time Depended Variation of the Molecular Weight and Polydispersity of Styrenated Oil in the RAFT Polymerization in 1,4-Dioxane at 90°C ([MI]/[PMDC] Mol Ratio: 1/4)

Time (h)	Conversion ^a (%)	Molecular weight ^b (M_n)	Polydispersity (PDI)
12	33.99	6230	1.41
24	39.49	8200	1.46
48	44.10	9020	1.52
100	54.10	10350	1.48

^a Conversion of styrene was determined gravimetrically.

^b Estimated by GPC based on polystyrene standards.

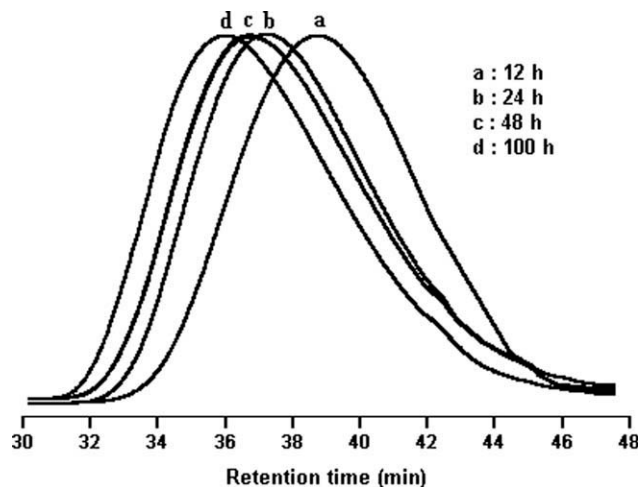


Figure 4 GPC curves for polymerization used 1,4-dioxane as a solvent at different intervals.

TABLE III
Conversion-Time Data and Time Depended Variation of the Molecular Weight and Polydispersity of Styrenated Oil in the RAFT Polymerization in Xylene at 90°C ([MI]/[PMDC] Molar Ratio: 1/4)

Time (h)	Conversion ^a (%)	Molecular weight ^b (M_n)	Polydispersity (PDI)
24	6.19	3970	1.44
72	17.6	4630	1.56
100	22.35	7930	1.45
300	55.45	11790	1.46

^a The conversion was monitored by gravimetric method.

^b Estimated by GPC based on polystyrene standards.

$7.5 \times 10^{-7} \text{ s}^{-1}$ and $1.11 \times 10^{-6} \text{ s}^{-1}$ for the polymerizations in xylene and 1,4-dioxane, respectively. This indicates that the polymerization in 1,4-dioxane is one and a half times faster than that in xylene.

Figure 7 shows GPC traces of the styrenated oil obtained in xylene for various reaction times. Although, at the end of higher reaction times (72 h, 100 h, 300 h), GPC curves of the samples are unimodal, at the lower reaction time (24 h), a shoulder appears on the GPC curve of the sample. This shows that the homogenization of the growing chain length could not be obtained in lower reaction times due to the heterogenous reaction medium.

Due to the living character of the RAFT process, further chain extension reaction with styrene was performed. This reaction was achieved in 1,4-dioxane at 90°C for 48 h. Increasing molecular weight of the original styrenated sample from $10,350 \text{ g mol}^{-1}$ (PDI: 1.48) to $33,670 \text{ g mol}^{-1}$ (PDI: 1.47) is clear evidence for the livingness of the applied RAFT process. For abbreviation, the chain extended polymer sample was denoted as SO-RAFT2-CE.

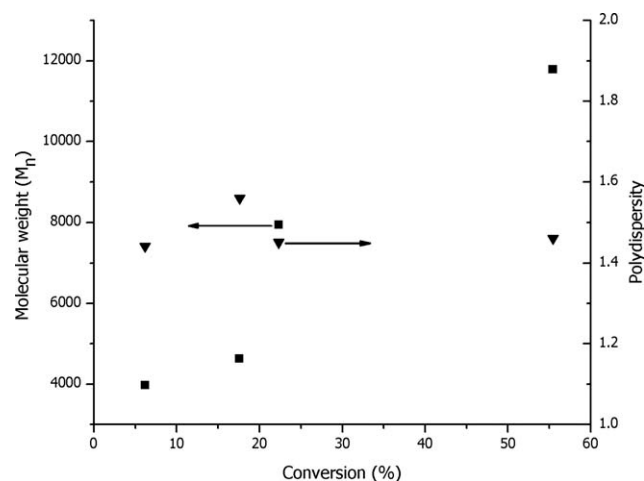


Figure 5 M_n -conversion (■) and PDI-conversion (▼) plots for the styrenation of oil by RAFT method in xylene at 90°C ([MI]/[PMDC]: [1/4]).

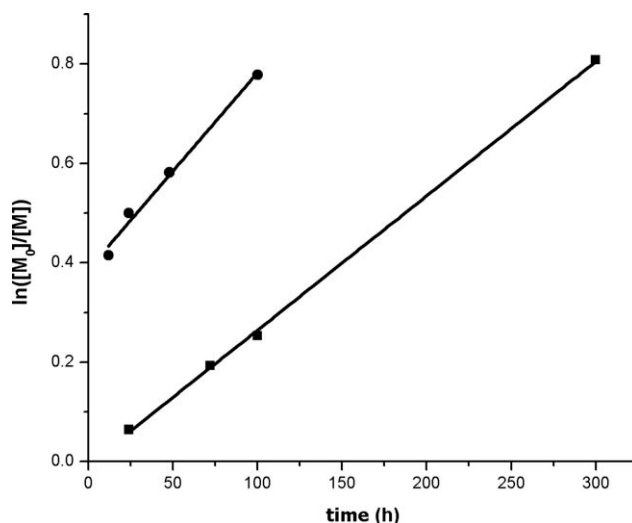


Figure 6 First order kinetic plots for styrenation of oil by RAFT method in 1,4-dioxane (●) and in xylene (■) solvents at 90°C.

For comparison, the styrenated oil was also prepared by using classical method.¹⁷ GPC trace of classical sample showed a bimodal distribution with a polydispersity of 2.71, due to uncontrolled polymerization and large amount of homopolystyrene formation.¹² For abbreviation, the sample prepared by classical procedure was denoted as SO-CLAS.

For the determination of film properties, thin films of SO-RAFT2 and SO-RAFT2-CE were prepared on the required substrates according to the test standards. The film properties (drying time, adhesion, flexibility, hardness, and resistance to acid, alkali and water) were determined and tabulated in Table IV. As shown, the adhesion (Tape test,

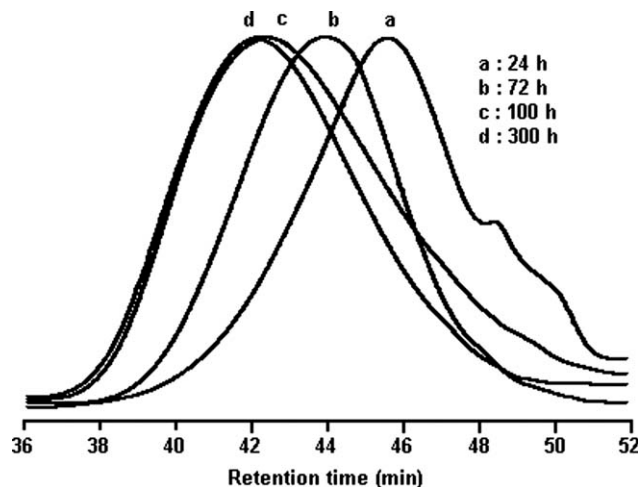


Figure 7 GPC curves for polymerization used xylene as a solvent at different time intervals.

TABLE IV
Film Properties of the Styrenated Oils Prepared under Controlled and Classical Conditions

Film properties	SO-RAFT2	SO-RAFT2-CE	SO	SO-CLAS*
Drying time ^a (Set to touch)	2 min 40 s	1 min 10 s	1.5 min	5 min
Adhesion ^b	2B	1B	0B	5B
Flexibility ^c	3 mm	5 mm	30 mm	2 mm
Water resistance ^d	no whiteness	no whiteness	70 min	5 min
Acid resistance ^e	nc	nc	nc	nc
Alkali resistance ^f	nc	nc	1 h 37 min	60 min
Hardness (Rocker Hardness)	52	51	82	42

* SO-CLAS was prepared by classical method.¹⁷

nc: no change (this states that the film did not undergo any deformation or corrosion).

^a The test was carried out at 25°C and 60% relative humidity.

^b Test method B was applied.

^c The diameter of the cylinder that caused no crack on the film.

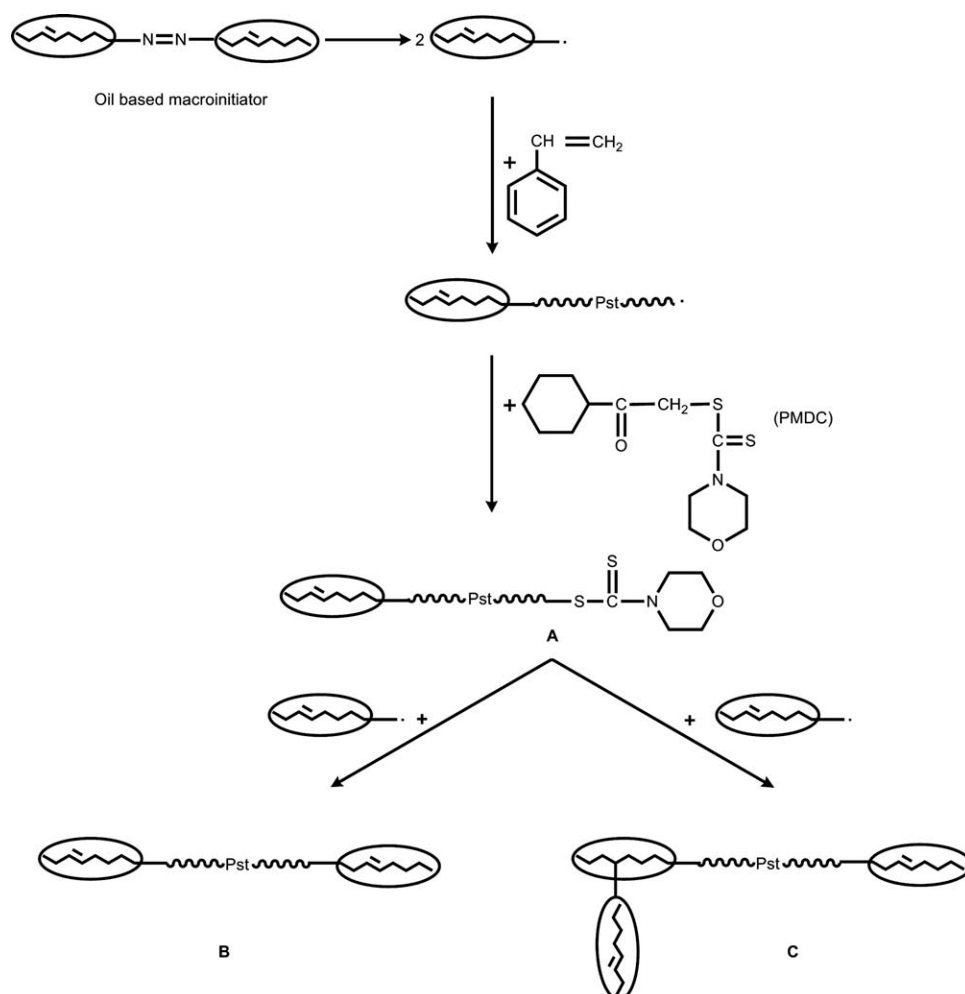
^d Time for disappearance of whiteness.

^e The test was carried out at 25°C with 9% H₂SO₄ solution during 24 h.

^f The test was carried out at 25°C with 5% NaOH solution during 24 h.

method B) of SO-RAFT2 and SO-RAFT2-CE were found to be 2B, 1B, respectively, and the adhesion of SO sample was found as 0B.

As shown in Table IV, flexibilities of SO-RAFT2 and SO-RAFT2-CE were also not satisfactory in comparison to that of SO-CLAS. To improve adhesion



Scheme 3 RAFT polymerization of styrene using MI and possible styrenated oil structures formed: polystyrene with oil molecules in one ends (A), in both ends (B) and incorporation of additional oil molecule via double bonds of sunflower oil (C).

TABLE V
The Film Properties of SO-MIMODRAFT2 Prepared by Post Reaction with MI

Drying time ^a	Adhesion ^b	Flexibility ^c	Water resistance ^d	Acid resistance ^e	Alkali resistance ^f	Hardness
2 min	5B	1 mm	no whiteness	nc	nc	34

nc: no change (this states that the film did not undergo any deformation or corrosion).

^a The test was carried out at 25°C and 60% relative humidity.

^b Test Method B was applied.

^c The diameter of the cylinder that caused no crack on the film.

^d Time for disappearance of whiteness.

^e The test was carried out at 25°C with 9% H₂SO₄ solution during 24 h.

^f The test was carried out at 25°C with 5% NaOH solution during 24 h.

and flexibility characteristics, SO-RAFT2 obtained for 12 h (Mn: 6230 g mol⁻¹, PDI: 1.41) was further reacted with the MI at 90°C for 48 h. For abbreviation, the sample modified by this treatment was denoted as SO-MIMODRAFT2. The molecular weight of this sample was found as 8000 g mol⁻¹ (PDI: 1.7) from GPC analysis. In this reaction, the primary radical generated by decomposition of MI is added to the styrene unit bearing dithiocarbamate end group as illustrated in Scheme 3. Additional inserting of oil moiety from MI to the polymer chains may be realized by the combination with the radicals generated on the fatty acid chains due to hydrogen abstraction, as shown in Scheme 3(C).

The film properties of SO-MIMODRAFT2 are explained in Table V. As shown, the adhesion and flexibility improved due to inserting of the oily portions to the structure by the addition free radicals generated through decomposition of MI. As a result, the styrenated oil with better film properties was obtained by the increment of oil content by further treatment of the polymer with MI.

CONCLUSIONS

Styrenation of oil was carried out for the first time successfully by RAFT process using PMDC as chain transfer agent. In this styrenation process, oil-based MI with labile azo groups was used as a starting material. In this way, the styrenated oil without homopolymer formation was obtained. Livingness of the process was evidenced by chain extension with styrene. The process gave relatively narrow molecular weight distributions (ca.1.5) in comparison to the styrenated oil prepared by the classical method.

Oil content of the polymer was increased by further reaction with primary radicals originating from the MI. The resulting oil rich polymer showed excellent film properties.

Regarding with those peculiarities of the films, the RAFT process presented for styrenation of oil might be of interest in producing oil-based coating materials in large scales.

References

- Gao, J.; Luo, Y.; Wang, R.; Li, B.; Zhu, S. J.; *Polym Sci Part A Polym Chem* 2007, 45, 3098.
- Smulders, W.; Gilbert, R. G.; Monteiro, M. J. *Macromolecules* 2003, 36, 4309.
- Chong, B. Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* 2003, 36, 2256.
- Vora, A.; Nasrullah, M. J.; Webster, D. C. *Macromolecules* 2007, 40, 8586.
- Luo, Y.; Liu, X. J. *J Polym Sci Part A Polym Chem* 2004, 42, 6248.
- Erkal, F. S.; Erciyas, A. T.; Yagci, Y. *J Coat Technol* 1993, 65, 37.
- Akbas, T.; Beker, U. G.; Guner, F. S.; Erciyas, A. T.; Yagci, Y. *J Appl Polym Sci* 2003, 88, 2373.
- Gultekin, M.; Beker, U. G.; Erkal, F. S.; Erciyas, A. T.; Yagci, Y. *Macromol Mater Eng* 2000, 283, 15.
- Kabasakal, O. S.; Güner, F. S.; Arslan, A.; Ergun, A.; Erciyas, A. T.; Yagci, Y. *J Coat Technol* 1996, 68, 57.
- Kabasakal, O. S.; Güner, F. S.; Erciyas, A. T.; Yagci, Y. *J Coat Technol* 1995, 67, 47.
- Güner, F. S.; Yagci, Y.; Erciyas, A. T. *Prog Polym Sci* 2006, 31, 633.
- Alemdar, N.; Erciyas, A. T.; Yagci, Y. *Prog Org Coat* 2009, 66, 99.
- Alemdar, N.; Erciyas, A. T.; Yagci, Y. *Prog Org Coat* 2010, 67, 55.
- Yağcı, Y. *Polym Commun* 1985, 26, 7.
- Yılmaz, O.; Baranak, M.; Güner, F. S.; Erciyas, A. T. *J Appl Polym Sci* 2005, 98, 1032.
- Cocks, L. V.; Rede, C. V. *Laboratory Handbook for Oil and Fat Analysts*; Academic Press: London and New York, 1966; p 120.
- Moad, G.; Rizzardo E.; Thang S. H. *Polymer* 2008, 49, 1079.
- Erkal, F. S.; Usta, S.; Erciyas, A. T.; Yagci, Y. *J Coat Technol* 2000, 72, 107.
- ASTM D 1640-03. Standard Test Methods for Drying, Curing, or Film Formation of Organic Coatings at Room Temperature. Annual Book of ASTM Standards 1991; Vol. 06.01, p 1.
- DIN 53152, Deutsche Normen, Deutscher Normenausschuss (DNA), October 1959.
- ASTM D 3359-90. Standard Test Methods for Measuring Adhesion by Tape Test, Test Method B, Annual Book of ASTM Standards; 1991; Vol. 06.01, p 511.
- ASTM D 2134-66. Standard Method of Test for softening of organic coatings by plastic compositions, Annual Book of ASTM Standards; 1991; Vol. 06.01, p 270.
- ASTM D 1647-89. Standard Test Methods for Resistance of Dried Films Varnishes to Water and Alkali. Annual Book of ASTM Standards; 1991; Vol. 06.01, p 236.
- Zhang, Z.; Zhu, X.; Zhu, J.; Cheng, Z. *Polymer* 2006, 47, 6970.