Use of the Surfmer 11-(Methacryloyloxy) undecanylsulfate MET as a Comonomer in Polystyrene and Poly(methyl methacrylate)

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Summary: The polymerizable surfactant sodium 11-(methacryloyloxy) undecanylsulfate (MET) has been synthesized with high purity, and its thermal stability and phase transitions have been studied by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. MET has been copolymerized in solution with methylmethacrylate (MMA) or styrene (S), initiated by azo-bis-isobutyronitrile (AIBN). The copolymers thus obtained have been studied by Gel Permeation Chromatography (GPC), Transmission Electron Microscopy (TEM), and DSC. Due to the incompatibility between the polar head of the MET units and the non polar S or MMA units, MET units organize in the amorphous polymer matrix and arrange in lamellar structures.

Keywords: copolymerization; differential scanning calorimetry (DSC); polymerizable surfactant; TEM

Introduction

"Surfmers" (polymerizable surfactants) behave like classical surfactants and self organize in aqueous solution prior to polymerization. Since the first attempts to polymerize polymerizable surfactants in aqueous media by Sherrington[1, 2] (which led to the formation of polysoap rather than polymerised micelles), surfmers have attracted considerable attention, mainly in emulsion polymerization and for templating polymerization[3-9]. In emulsion polymerization, for example, they reduce most of the disadvantages associated with the use of classic surfactants, such as flocculation, high permeability of polymer film and water retention, while advantageously increasing the stability of the latex during storage. Thus, surfmers

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have been used for the preparation, in microemulsion, of size-controlled polymer particles on different scales (micro to nanometer)[10-19]. Surprisingly, only a few authors have reported on the organization of surfmers in bulk when copolymerized with a non surface-active comonomer. Favresse et al[20, 21] described the formation of super-structures in bulk with polymerized or copolymerized zwitterionic surfmers: poly(carbobetaine)s can form lamellar or interdigitated structures, depending on their chemical structure. When copolymerized with N-vinylpyrrolidone or dimethylacrylamide, carbobetaines based on isobutylene form lamellar phases in bulk[20]. In this last example, the copolymers contain a high ratio of surfmers (about 45 to 70 mol%).

To our knowledge, there are no reports in the literature on copolymers containing low ratios of surfmer units that form supramolecular structures in bulk (eg. lamellar structures). In this work, we prepared copolymers of styrene (S) and copolymers of methylmethacrylate (MMA) containing a low ratio of the surfmer sodium 11-(methacryloyloxy) undecanylsulfate (MET). We chose MET as the surfmer because its synthesis is known, it is readily polymerizable, and copolymerizable with S or MMA.

Pursuing the objective to determine the role played by MET in the organization in bulk when copolymerized with S or MMA, we describe here the synthesis and the properties of PS and PMMA containing 1.5 to 6 mol% of MET units. Properties were determined by differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA) and transmission electron microscopy (TEM). The thermal behaviour of the polymerizable monomer MET was studied by DSC, TGA, and microscopy under cross-polarized light.

Experimental

Azo(bis)isobutyronitrile (AIBN) was recrystallized from methanol. S and MMA were distilled prior to use. MET was synthesized according to a procedure described in the literature[22].

GPC analysis of the copolymers was performed on a Waters 510 HPLC. A PL-ELSD 1000 (light scattering) detector and a PL-gel Mixed A column were used. A sample

concentration of 1 mg/ml and eluent flow of 1 ml/min were used. All measurements were performed at 50 °C in dimethylformamide (DMF). Differential scanning calorimetry (DSC) was done using a DSC22C (Seiko II), at a heating rate of 10 °C/min.

Copolymerizations were done by dissolving 1 wt% AIBN in chloroform at 70 °C. 2.0g (0.019 mol) of S or MMA and 5, 10, or 20 wt% MET were dissolved in chloroform and added dropwise over 10 min to the solution of the initiator. The reaction mixture was then refluxed for 4 h at 70 °C. The polymer obtained was precipitated in methanol and dried under reduced pressure.

Monomer MET

A convenient approach to the synthesis of a polymerizable surface-active molecule is to attach the polymerizable group to the hydrophobic tail first, leaving the insertion of the head group to the end of the reaction sequence. Using this method, many practical problems frequently associated with isolation and purification of surface-active intermediates are avoided. Methacrylic acid and 11-bromoundecanol were used as starting material for the preparation of 11-(methacryloyloxy) undecanol. Methacrylic acid was firstly deprotonated with sodium hydroxide to give the corresponding sodium acrylate. 11-(methacryloyloxy) undecanol was obtained from the 11-bromoundecanol and sodium methacrylate using phase-transfer-catalyst conditions. The obtained alcohol was then sulfonated with neat chlorosulfonic acid, and the resulting product quenched with sodium carbonate to obtain the MET. Results of ^{1}H-, and ^{13}C-NMR, and elemental analysis showed that the MET was >95 % pure.

Analysis of MET by TGA showed two distinct stages of degradation. The onset T_{on} and maximum T_{max} temperatures of the first step (219.2 and 250.2 °C), and the second step (322.2 and 411.0 °C) are illustrated in Fig. 1. The maximum in the weight loss observed reached 0.89 g/min at T_{max}.

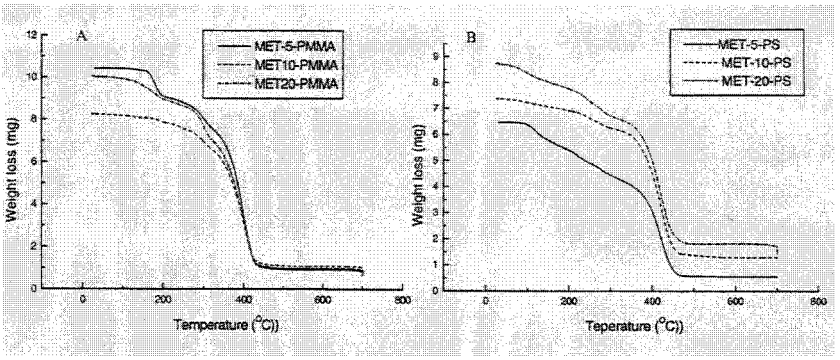

Figure 1. TGA of the monomer MET

DSC analysis of MET displayed two distinct transitions for the first heating cycle, see Fig. 1, which reveals thermotropic behaviour. Although the precise nature of the mesophase observed has not been determined in this work, we assume that the MET monomer forms a liquid crystalline phase and not Condis-cristals[23, 24] between the two-phase transitions. The crystal to liquid-crystal transition appears at 57.1 °C, followed by the clearing point transition at 85.5 °C. The cooling cycle shows a crystallization transition at T_c=74.7 °C, which cannot be assigned to a specific phase transition due to supercooling and partially to hysteresis attributable to the temperature scan rate. The second heating cycle (see Figure 2) confirms the reproducibility of the two transitions observed in the first heating cycle. There was however a slight shift in the temperatures of the transitions (53.6 and 84.1 °C). In addition, the enthalpies of melting are smaller for the second heating than for the first heating, due to the loss of crystallinity occurring during the first heating cancelling any thermal history (see Table 1). The observation of MET by microscopy under cross-polarized light, with heating stage, confirmed the existence of the mesophase. When the sample is heated from room temperature, a change in crystal texture occurs from 54 to 88 °C. The mesophase is stable from 88 to 107 °C, thereafter it becomes transparent as the temperature increases. The sample is totally isotropic at 152 °C. When cooled, the MET forms a fan-like texture below 110 °C.

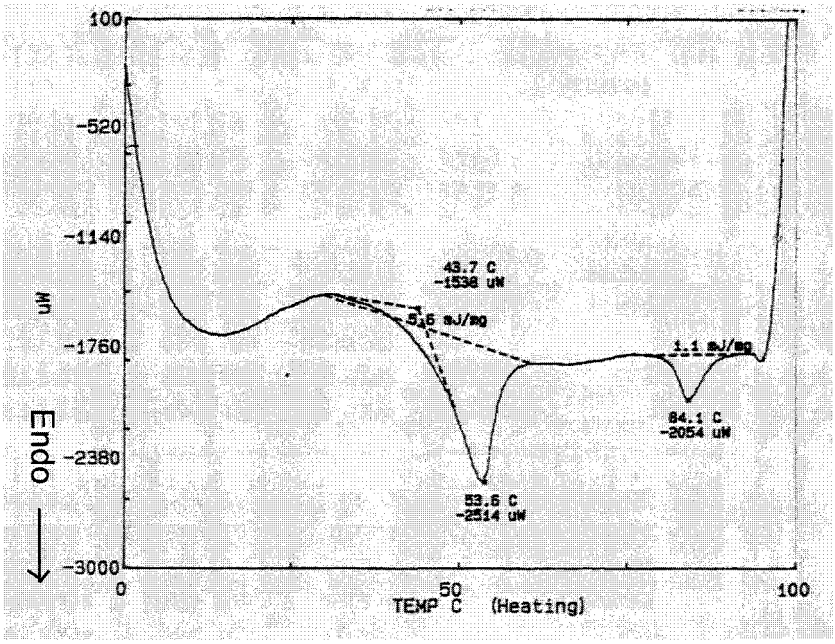

Figure 2. DSC of the monomer MET

Table 1. DSC data of the monomer MET

	Temperature (°C)		Enthalpy (KJ/mol)
First heating	T_m	57.1	15.2
	T_{cl}	85.5	1.2
Cooling	T_c	74.7	-0.5
Second heating	T_m	43.7	2.0
	T_{cl}	84.1	0.4

Copolymers

The copolymerisation of surfmers with non-polar comonomers such as S or MMA is generally performed in emulsion[25-27]. Accordingly, the surfmer MET has been copolymerized in emulsion with various comonomers, including S[17, 22]. Because the objective of our work was to determine the role played by the MET comonomer on the properties of PS and PMMA in bulk, we intentionally synthesized the copolymers

by free-radical polymerization in solution and not in emulsion, so as to prevent any self-aggregation of the surfmer prior to polymerization. The solvent used (chloroform) dissolved both comonomers well, and aggregates were not formed by the surfmer. The reactivity ratios of MET with S and with butyl acrylate have been reported by Otsu[28] and Urretabizkaia[29] (see Table 2). From these values (0.53 and 0.30 respectively, for r_S and r_{MET}), one can assume that the MET-S copolymers are random copolymers, with a tendency to alternate. On the other hand, for the copolymers of MMA, we did not deduce the distribution of the comonomers because of the lack of data in the literature about the reactivity ratios of comparable comonomers.

Table 2. Reactivity ratios of MET with styrene and butyl acrylate[22]

	Styrene (S)[28]		Butyl Acrylate (BA)[29]	
Reactivity ratios	r_S	r_{MET}	r_{BA}	r_{MET}
	0.53	0.30	0.32	2.6

After purification of the copolymer by precipitation in methanol, the yields obtained reached only 20 %. The copolymerization products, MET-PS and MET-PMMA, were characterized by FT-IR. All purified samples showed residual amounts of monomer left in the copolymer as determined by the presence of a very small vibration band for the carbon-carbon double bond at about 1650 cm^{-1} in the FT-IR spectrum. The sensitivity of the FR-IR method did however not permit the accurate determination of the ratio of monomer left in the copolymer. Typical infrared spectra that are representative of MET-PS and MET-PMMA are shown in Figs. 3 and 4, respectively. A summary of the assignment of bands representative of both types of copolymers is given in Table 3. The amount of incorporated MET was assessed from the ratio between the integrated areas of the carbonyl band centred around 1720 cm^{-1} and the –C-O- band around 1144 cm^{-1} (for copolymers with PMMA) or the aromatic band at 697 cm^{-1} (for copolymers with PS) after correction by "attenuated total reflexion". The copolymers displayed an increase in the ratio of integrated areas as the amount of MET was increased (see Table 4). Because the accuracy of the FT-IR was insufficient, we considered that the ratio of MET in the copolymers is equal to the ratio of the monomer MET fed for the polymerization.

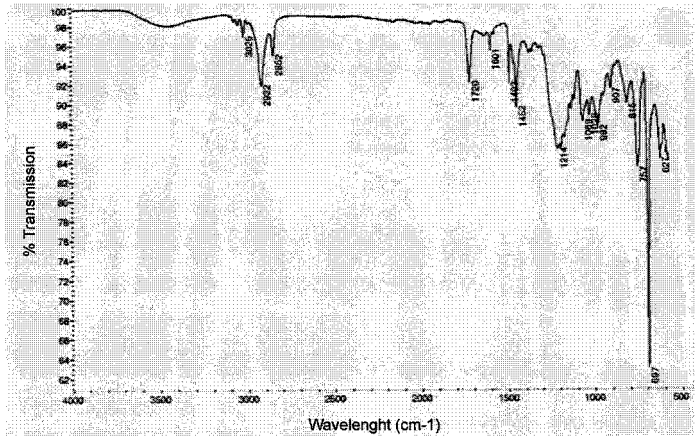

Figure 3. Typical FT-IR spectrum of the MET-PS copolymers

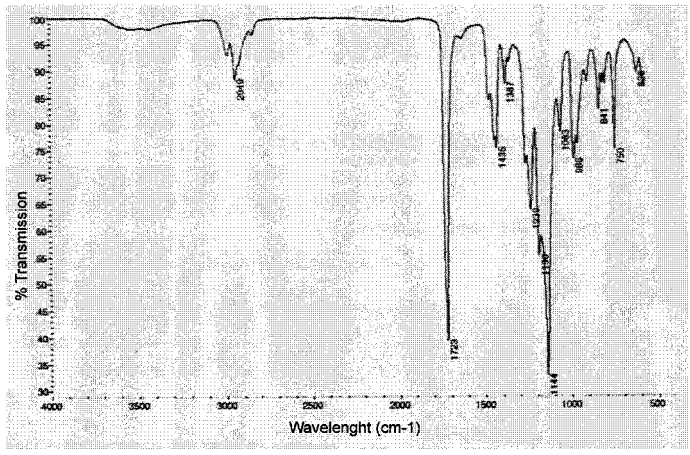

Figure 4. FT-IR spectrum of MET-PMMA

Table 3. FT-IR band assignments for copolymers MET-PS and MET-PMMA

	Poly(S-co-MET)	Poly(MMA-co-MET)
Assigned group	Wavelength (cm-1)	Wavelength (cm-1)
-CH2-	3026, 2923, 2853	2994, 2949, 2857
-O-C=O	1720	1723
Aromatic ring	1601	-
Aromatic ring	1493	-
-CH2-	1452	1435
-CH3	1387	1387
-C-O-	1213	1239, 1144
-SO2O-	1069	1063
Aromatic ring	757, 697, 627	-
-CH2-	815	841, 750

Table 4. Ratios of MET monomer units determined from the FT-IR band ratio

copolymer	FT-IR band ratio
MET-1.5-PMMA	0.922
MET-3-PMMA	0.949
MET-6-PMMA	1.041
MET-1.5-PS	0.665
MET-3-PS	0.671
MET-7-PS	1.438

Concerning the solubility of the copolymers: we observed that they remained in solution after the copolymerization reaction, although, after precipitation, the dried copolymers would not re-dissolve in chloroform. This behaviour has been reported before[1, 30, 31], even in the case of polymers, which appear to be initially fully soluble. It seems that in the dry state the ionic groups are tightly bound within a hydrophobic network. Indeed, they may form microphase-segregated domains[1]. The product has trouble dissolving after precipitation and drying, even after a prolonged dissolution

time. Copolymers of mixed polarity are known for their solubility problems, as one of the comonomer is very polar and the other is non-polar[30]. MET is soluble in polar solvents, whereas PMMA and PS are soluble in non-polar solvents. Both series of copolymers were insoluble in the following solvents: water, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, methanol, dichloromethane, chloroform, acetone, 1-methyl-2-pyrrolidone and hexafluoro-2-propanol. Toluene, m-cresol and chlorobenzene only swelled the samples. The Samples were soluble only in tetrahydrofurane (THF) or in DMF after being heated at 80 °C and stirred for 24 h.

The determination of the average molecular weight of the copolymers was performed by GPC in THF. Most of the chromatograms displayed an unusual tri-modal distribution (see Fig. 5 for example). The molecular weights calculated for each copolymer, using a PS calibration curve, are summarized in Table 5.

It was observed that the very high molecular weight fraction has a narrow molecular weight distribution, while the fraction with medium molecular weight has a broad molecular weight distribution. The narrow molecular weight distribution is because the column has an exclusion limit above 10 7g/mol, and macromolecules of bigger size are totally excluded. The lower molecular weight distribution is broader, which is more in accordance with the free radical mechanism of the copolymerization. It can be speculated that the two very high molecular weight distributions arise from the formation of aggregates when the copolymer is in solution. In order to determine whether aggregations occur at these extremely high molecular weights, fractions were taken at the different peak elution times in order to investigate the chemical composition of each fraction. The different fractions were analysed by FT-IR. Fractions of both low and intermediate molecular weights displayed similar spectra to that of the dry copolymer sample. On the other hand, the fraction with the very high molecular weight distribution exhibited an absorption band at 1659 cm-1, indicating the presence of a carbon-carbon double bond. This shows that a residual amount of MET monomer forms micelles or aggregates with the copolymer, giving rise to the presence of the high molecular weights distributions. Moreover, the intermediate molecular weight probably arises from aggregation of copolymers in THF.

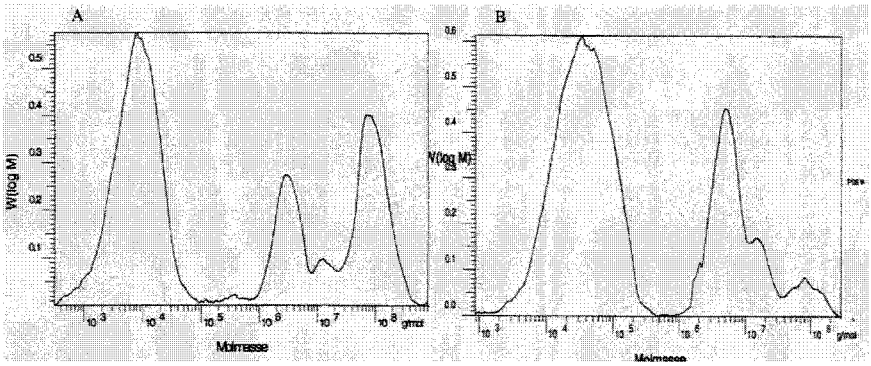

Figure 5. Typical molecular weight distribution for (A) MET-10-PS and (B) MET-10-PMMA

It was observed that the very high molecular weight fraction has a narrow molecular weight distribution, while the fraction with medium molecular weight has a broad molecular weight distribution. The narrow molecular weight distribution is because the column has an exclusion limit above 10^7 g/mol, and macromolecules of bigger size are totally excluded. The lower molecular weight distribution is broader, which is more in accordance with the free radical mechanism of the copolymerization. It can be speculated that the two very high molecular weight distributions arise from the formation of aggregates when the copolymer is in solution. In order to determine whether aggregations occur at these extremely high molecular weights, fractions were taken at the different peak elution times in order to investigate the chemical composition of each fraction. The different fractions were analysed by FT-IR. Fractions of both low and intermediate molecular weights displayed similar spectra to that of the dry copolymer sample. On the other hand, the fraction with the very high molecular weight distribution exhibited an absorption band at 1659 cm^{-1}, indicating the presence of a carbon-carbon double bond. This shows that a residual amount of MET monomer forms micelles or aggregates with the copolymer, giving rise to the presence of the high molecular weights distributions. Moreover, the intermediate molecular weight probably arises from aggregation of copolymers in THF.

Table 5. Molecular weight of MET-PS and MET-MMA copolymers, determined by GPC (standard PS)

Copolymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n
MET-1.5-PMMA	383 000	543 000	1.42
	215 000	368 000	1.71
	160 000	528 000	3.29
MET-3-PMMA	758 000	950 000	1.25
	481 000	793 000	1.65
	203 000	515 000	2.53
MET-6-PMMA	574 000	204 000	3.56
	132 000	403 000	3.05
MET-1.5-PS	407 000	689 000	1.69
	893 000	205 000	2.30
	332 000	108 000	3.24
MET-3-PS	612 000	105 000	1.71
	244 000	381 000	1.56
	473 000	133 000	2.82
MET-7-PS	678 000	965 000	1.42
	102 000	294 000	2.89
	394 000	919 000	2.33

The thermal stability of the copolymers was determined by TGA. All the samples showed a multi-step weight loss. The first weight loss was gradual, with an onset at about 100 °C (which is probably due to water bound to the sodium sulfonate groups of MET). The onset of the second weight loss appeared at about 300 to 400 °C, which shows up the onset of the real degradation of the copolymers. As expected for the MET-PS copolymers, the residual weight of the samples after being heated at 700 °C increases as the MET ratio increases, because of the higher content of sulphur and sodium. Nevertheless, one should note that the residual weight observed for the MET-PMMA copolymers were unchanged with the ratio of MET.

The thermal behaviour of the copolymers, as studied by DSC, showed a weak melting transition on the heating curves, while no T_g could be detected. Due to the weakness of the energies of the transitions, we have reported only the maximum temperature in Table 6 (including the crystallization temperatures observed while cooling the samples). Because PMMA and PS are amorphous, both melting and crystallization temperatures probably come from some organization of the MET monomer units. Due

to the strong thermodynamic incompatibility between the PS matrix and the ionic polar head of the polymerized MET, it is believed that the transitions (melting and crystallization) observed originate from associations of the ionic heads of the copolymerized MET surfmers. Such behaviour has been previously reported for similar copolymers containing a carboxylate polar head with a divalent counter-cation M^{2+} [32].

Table 6. Temperatures of melting (T_m) and crystallization (T_c) of MET-PS and MET-MMA copolymers, determined by DSC

Copolymer	T_m (°C)	T_c (°C)
MET-1.5-PS	174.0	125.6
MET-3-PS	141.9	119.6
MET-7-PS	144.7	118.7
MET-1.5-PMMA	148.3	122.5
MET-3-PMMA	144.9	125.4
MET-6-PMMA	138.3	102.5

TEM of a 50 nm microtomed sample of MET-7-PS is shown in Figure 6. A lamellar nano-structure is formed, with spacing between the lamellae around 3 nm. Note that the expected nano-structure thickness should be around 3.8 to 4 nm if the lateral chains of the MET units are considered stretched (which is unlikely). Moreover, from the texture of the TEM picture, the organization of the surfmer repeat units could be considered as bead-like structures, so that the order is not perfectly lamellar but incorporates spheroid structures as well. Due to the thermodynamic incompatibility between the polar heads of the MET and the PS matrix, and taking into account the structure observed by TEM, one can speculate that the MET repeat units self assemble via the formation of intermolecular bridges (see Figure 7).

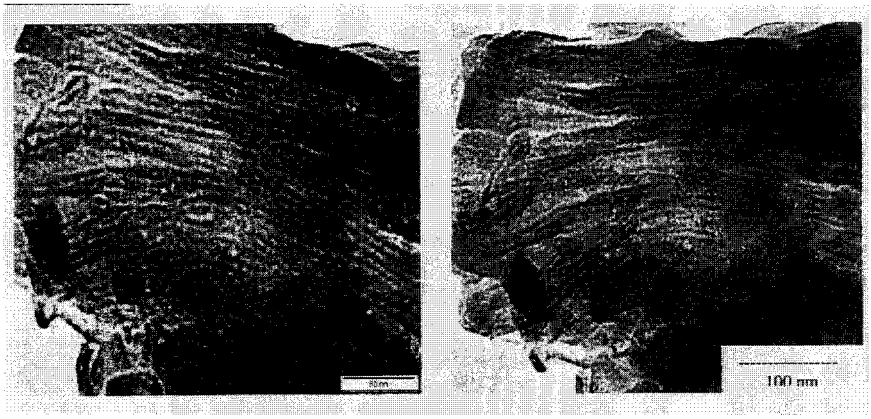

Figure 6. TEM pictures of MET-7-PS

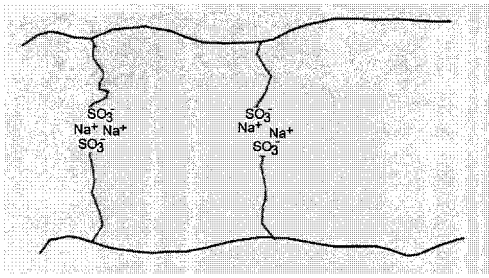

Figure 7. Interchain interactions between the ionic heads of the MET monomer units

Conclusion

The monomer MET was synthesized an its thermal behaviour studied by TGA, DSC, and microscopy under cross-polarized light. It presents a thermotropic behaviour, with a mesophase stable from 88 °C up to 107 °C.

Pursuing the objective to study the organization of MET in a non-polar amorphous polymer matrix, two series of copolymers that contained 1.5 to 6 mol% of MET units and S or MMA were successfully synthesized. The resulting copolymers displayed a weak thermal transition that can be assigned to the organization of the side chain of the MET monomer units in the amorphous polymer matrix. Furthermore, and despite of the low MET content, MET monomer units self assemble in pseudo-lamellar

structures. This is occurring because of the incompatibility between the MET sulfonate groups and the non-polar polymer matrix.

Acknowledgments

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