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Abstract: Hybrid organic-inorganic films have been prepared through a dual-cure process, involving photopolymerization (UV-curing) of a methacrylic resin and hydrolysis/condensation of alkoxysilane groups, in the presence of three different liquid crystalline oligomers bearing acrylic reactive groups and synthesized on purpose. These UV-curable mixtures have been coated on glass substrates, exposed to UV radiation in inert (nitrogen) atmosphere, then thermally treated in order to promote the occurrence of the sol-gel reaction and finally peeled off from the substrate. The morphology of the obtained films has been investigated by means of SEM, ESEM and AFM measurements. Significant silica enrichment on the "gas side" of the films (i.e. the side exposed to the UV-radiation) has been found, as well as the occurrence of the formation of interesting silica conical shapes on the same side with respect to the glass counterpart. Because of the constraints exerted by the inorganic domains on the mobility of the polymer chains, the Tg values of the obtained networks have been found to increase in the presence of the silica phases, which also might have contributed to the occurrence of segregation phenomena of the liquid crystalline phases.

Highlights

- Three liquid-crystalline (LC) acrylic oligomers were synthesized
- Hybrid organic-inorganic films containing the LC units were prepared
- An asymmetric distribution of silica on the surfaces of the films was assessed
- Silica conical shapes preferably on one side of the hybrid LC films were formed

Hybrid organic-inorganic UV-cured films containing liquid-crystalline units

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ABSTRACT

Hybrid organic-inorganic films have been prepared through a dual-cure process, involving photopolymerization (UV-curing) of a methacrylic resin and hydrolysis/condensation of alkoxy silane groups, in the presence of three different liquid crystalline oligomers bearing acrylic reactive groups and synthesized on purpose. These UV-curable mixtures have been coated on glass substrates, exposed to UV radiation in inert (nitrogen) atmosphere, then thermally treated in order to promote the occurrence of the sol-gel reaction and finally peeled off from the substrate. The morphology of the obtained films has been investigated by means of SEM, ESEM and AFM measurements. Significant silica enrichment on the “gas side” of the films (i.e. the side exposed to the UV-radiation) has been found, as well as the occurrence of the formation of interesting silica conical shapes on the same side with respect to the glass counterpart. Because of the constraints exerted by the inorganic domains on the mobility of the polymer chains, the T_g values of the obtained networks have been found to increase in the presence of the silica phases, which also might have contributed to the occurrence of segregation phenomena of the liquid crystalline phases.

Keywords: Hybrid organic/inorganic films; Dual-cure processes; Liquid-crystalline acrylic oligomers; Silica phases; Morphology.

1. Introduction

As already well described in the literature, hybrid organic/inorganic materials (also known as *ceramers* or *ormocers*) exhibit a peculiar morphology, where an organic phase is strictly interconnected with an inorganic one; sometimes, the formation of strong covalent bonds is achieved by using a coupling agent, able to react with both the phases [1-17]. As a consequence, these materials provide to conjugate the attractive properties of ceramics, such as thermal stability, high modulus and low coefficient of thermal expansion, with the high ductility and low temperature processing conditions of polymers, thus widening their potential applications. Indeed, in these hybrid materials, the presence and morphology of the inorganic nanophases homogeneously dispersed within the polymer matrix strongly affect their final features, such as perfect transparency, high mechanical properties, good surface properties, thermal resistance, flame retardancy and barrier properties [18-28]. Therefore, some of their applications may concern optical, mechanical, electronic and biomedical fields; at present, their main commercial application is in the field of protective coatings for different organic and inorganic substrates (like clear scratch-resistant automotive coatings), adhesives and moisture-cure room-temperature vulcanizing sealants [29].

Several hybrids based on silica and different polymeric matrices have been prepared so far; usually, their synthesis is carried out through the sol-gel technique, which consists of a two-step hydrolysis and condensation reaction starting from (semi)metal alkoxides (tetramethoxysilane, tetraethoxysilane, etc.). When sol-gel processes are combined with polymerization reactions, organic-inorganic networks strictly interconnected are built, leading to the formation of nanostructured phases with a very high degree of dispersion.

Silica/poly- ϵ -caprolactone hybrids were prepared and deeply investigated by Jerome and coworkers [5-8]. Pilati and coworkers investigated similar systems, evidencing their flame retardancy and barrier properties [30]. Silica/polyacrylates [31] and silica/polyimide [32,33] hybrid materials having outstanding thermal stability were also studied.

Recently, Kanezashi et al. have prepared organic–inorganic hybrid silica membranes with controlled silica network size using bis(triethoxysilyl) ethane as precursor of the inorganic phase; single-gas permeation and binary-component gas separation characteristics for the hybrid silica membranes were examined in a wide temperature range (100–300°C) [34]. Bang and Kim have exploited sol-gel processes for synthesizing hybrid coatings based on poly(lactic acid) and silica with improved oxygen barrier properties by using sol–gel methods [35]. Sol-gel derived hybrid epoxy acrylate coatings have been also prepared by Xiao and Hao, who demonstrated an increased thermal stability of the hybrid system with respect to the pure organic counterpart [36].

Hybrid epoxy–silica polymer films based on Diglycidylether of Bisphenol A (DGEBA) resin and diamine curing agent have shown excellent thermal stability, superior dynamic storage modulus, and higher glass-transition temperatures as compared with the pure epoxy system [37]. Very recently, hybrid organic-inorganic systems have been also exploited for transparent Organic Light-Emitting Diodes encapsulation [38] and for obtaining very smooth, transparent, hydrophobic and oleophobic coatings, usable to modify different kinds of substrates [39]. As far as liquid crystalline networks are considered, Ober and coworkers have thoroughly investigated their behavior both as elastomers and thermosets [40,41].

In this context, dual-cure processes, which combine the sol-gel technique with a UV-curing reaction, can be exploited for preparing hybrid organic/inorganic materials [42]: indeed, hybrid organic-inorganic nanocomposite systems based on vinyltriethoxysilane, tetraethoxysilane and polyfunctional acrylates have been reported in the literature [43,44]. We have also synthesized some hybrid materials starting either from epoxy [45-47], vinyl ether [48], or (meth)acrylic resins [49-51], in order to get the advantages connected to both the curing methods, such as thermal stability, barrier and mechanical properties.

The use of liquid crystalline structures in the formulation of hybrid organic-inorganic coatings is quite limited. Quite recently, Nishizawa et al. succeeded in synthesizing a liquid crystalline organic–inorganic hybrid, consisting of an azobenzene derivative and titanium oxide: this film was

then subjected to the inscription of surface relief structure formation by patterned UV irradiation. The efficiency of the phototriggered mass transfer showed a clear temperature dependency [52].

Wiesner and coworkers prepared nanohybrids from liquid crystalline extended amphiphilic dendrimers, where these latter were exploited as structure-directing agents for generating silica nanostructures [53]. Liquid crystalline structures have also been exploited for the preparation of hybrid organic-inorganic materials to be used for electrolytic membranes for fuel cells [54].

In this work we have considered photopolymerizable acrylic oligomers, which have been subjected to dual-cure processes in the presence of (i) different LC oligomers bearing methacrylic reactive groups and synthesized on purpose, (ii) tetraethoxysilane, as the precursor of the silica phase and (iii) a coupling agent (methacryloyl-oxypropyl-trimethoxysilane), able to form covalent bonds in between the inorganic and polymer phases. These mixtures have been subjected to the photopolymerization reaction involving methacrylic double bonds, then to a thermal condensation of the alkoxysilane groups.

Scanning Electron Microscopy (SEM), Environmental Scanning Electron Microscopy (ESEM) and Atomic Force Microscopy (AFM) microscopy have been exploited for thoroughly investigating the morphology of the obtained hybrid films. Finally, their thermal behaviour has been assessed through Differential Scanning Calorimetry (DSC) measurements and correlated with the composition of the coatings.

2. Materials and Methods

2.1. Materials

All solvents and reagents (methacrylic acid, aniline, Bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA), methacryloyl-oxypropyl-trimethoxysilane (MEMO), tetraethoxysilane (TEOS), hydrochloric acid and dibutyltin diacetate (condensation catalysts)) were purchased from Aldrich and used as received. As photoinitiator, 2-hydroxy-2-methyl-1-phenyl propan-1-one (Darocur 1173 from BASF) was employed.

DGEBA was purchased as Epikote 827 (Equivalent weight per epoxy=182); 4,4'-diglycidyloxybiphenyl (DIF) was synthesized as previously reported [55].

The structures of BEMA and MEMO and of the photoinitiator are reported in Figure 1; n is approximately equal to 15.

2.2 Synthesis of the LC oligomers

The LC oligomers were prepared by reaction of a mesogenic diepoxy compound with aniline (which acted as a chain extension agent) and methacrylic acid (MA). The stoichiometric ratio between the difunctional reagents, epoxy and aniline, was selected in order to obtain an epoxy-terminated compound, which contained respectively the average of two epoxy monomers and one amine monomer (LC1), three epoxy monomers and two amine monomers (LC2 and LC3). The elongated epoxy was then reacted with an excess of methacrylic acid in order to replace the epoxy end groups with methacrylic functionalities. As an example, the structure of LC1 is schematized in Figure 1.

In a typical preparation of LC1, 6.71 mmol DIF and 4.48 mmol aniline were dissolved in 20 mL 1,4-dioxane (Aldrich, 99%) at 50°C. 5 drops of glacial acetic acid (Aldrich, 99.7%) were added and the mixture was kept at reflux for two hours and then cooled down to room temperature. 4.9 mmol MA, 3 drops of N,N-dimethylbenzylamine and 2 milligrams of hydroquinone (acting as a radical scavenger) were added. The resulting mixture was refluxed for one hour, then cooled down to room temperature and poured in n-hexane, whereupon a creamy precipitate was obtained, filtered, washed with n-hexane and vacuum dried for 5 hours. Yield: 78%.

¹H Nuclear Magnetic Resonance (NMR) (^dDMSO, tetramethylsilane, δ , ppm): 7.55-7.51(m, Ar); 7.08 (m, Ar); 7.02-6.98 (m, Ar); 6.60 (m, Ar); 6.07 (t, acrylic); 5.68 (t, acrylic); 4.37-3.97 (m, CH₂ and CH adjacent to ester and ether oxygens and to hydroxyl groups); 3.84-3.35 (dm, CH₂ adjacent to nitrogen); 2.02 (d, OH); 1.88 (d, CH₃ on acrylic). ¹³C NMR (^dDMSO, tetramethylsilane, δ , ppm): 167.0 (C=O); 157.4, 128.9, 127.3, 114.9 (Ar of DIF); 150.0, 130.1, 118.0, 112.1 (Ar of Ani); 126.0

(CH₂ acrylic); 69.0 (CH₂ adjacent to O-Ph); 66.7 (CH₂ adjacent to methacrylic); 65.7 (CHOH); 62.1 (CH₂ adjacent to nitrogen); 18.0 (CH₃ on acrylic).

A similar procedure was followed for synthesizing LC2 and LC3 monomers, but changing the amounts of DIF, Ani and MA as follows:

- LC2: DIF, 6.71 mmol; Ani, 3.35 mmol, MA, 3.7 mmol. Yield: 81%.
- LC3: the epoxy compound consisted of a mixture of 4,4'-diglycidyloxybiphenyl (DIF) and DGEBA (molar ratio 2:1); therefore, 6.71 mmol DIF, 3.35 mmol DGEBA, 6.73 mmol Ani and 7.40 mmol MA were used. Yield: 53%.

Molecular weights were estimated by ¹H NMR spectra, from the comparison of the integrated areas of the signals at 6.07, 5.68 and 1.88 ppm (acrylic protons and methyl on acrylic group), 7.0 and 7.5 ppm (aromatic from DIF), 6.6 ppm (aromatic from Ani) and eventually 1.56 ppm (methyl of DGEBA). The estimation gave the following values: LC1, 1976 g/mol; LC2, 2194 g/mol; LC3, 2090 g/mol.

2.3 Preparation of the hybrids coatings

A typical UV-curable mixture was prepared by adding MEMO (20 wt.% with respect to BEMA), the LC oligomer and TEOS to BEMA monomer; the obtained mixture was added of 4% of Darocur 1173 as photoinitiator, 7% of water (alkoxy/water molar ratio= 2) and 1% of both dibutyltin diacetate and HCl conc., as condensation catalysts. Then it was coated on a glass substrate, using a 100 µm wire wound applicator. The composition of the liquid UV-curable mixtures is reported in Table 1: hereafter, the different final materials will be coded as LCXSY, where X represents the type of LC oligomer and Y ranges from 1 to 4 according to Table 1.

The photochemical curing was performed by using a medium vapor pressure Hg UV-lamp (Helios Italquartz, Italy), with radiation intensity on the surface of the sample of 40 mW/cm², working in N₂ atmosphere. Three not consecutive 30 s exposures to the UV irradiation were carried out. The subsequent condensation reaction was performed treating the photocured films in an oven at 75°C

for 4 h. The silica content after this thermal treatment was in agreement with the composition of the UV-curable mixtures, as assessed by TGA analysis [49].

2.4 Characterization techniques

^{13}C and ^1H NMR spectra were recorded at 75.463 and 300.066 MHz, respectively, on a VARIAN GEMINI (6.1B version), with the applied magnetic field of 7.0 T for 300 MHz with proton noise decoupling for ^{13}C . The spectra were recorded at room temperature with 10-20% (w/v) sample solutions in dimethylsulphoxide- d_6 . The chemical shifts were given in ppm from tetramethylsilane using the appropriate shift conversions.

Calorimetric studies (DSC) were performed using a QA1000 apparatus (TA Instruments) from -80 to 200°C, with a heating rate of 10 K/min. The equipment was previously calibrated with Indium (156.6°C) and Zinc (419.58°C) pearls.

SEM analyses were carried out using a LEO-1450VP Scanning Electron Microscope on the cross-sections of the hybrid films fractured in liquid nitrogen. Coating pieces (0.5 mm×0.5 mm) were fixed to conductive adhesive tapes and gold-metallized. The morphology of the hybrid films was also investigated in low vacuum by means of an ESEM FEI-Quanta 600 apparatus, without any metallization. The apparatus was coupled with Oxford Inca equipment for Energy-Dispersive X-ray (EDX) analysis. The obtained images were exploited for assessing the formation of silica clusters and the silica distribution on the two sides of the films.

AFM images were recorded with an Agilent 5500 Environmental Atomic Force Microscope (Agilent Technology, USA) equipped with an extender electronics module, which enables phase imaging in Tapping ModeTM. All the images were recorded in tapping mode using Multi 75 (BudgetSensors, USA) silicon cantilevers (Length 225 μm , width 28 μm , thickness 3 μm) with a force constant 3 N/m and a resonance frequency 75 kHz. The scan rate was typically 0.7-2 Hz. All the images were measured at room temperature, in air, without filtering. The microscope was placed on an active vibration isolation chamber (Agilent Technology, USA), which was further placed on a

massive table for eliminating external vibration noise. The Nanotec WSxM 5.0 Develop 4.0 – Image Browser Scanning Probe Microscopy Software was used for the roughness analysis of the images. [56]

Textures and clearing temperatures of the samples were observed by polarized optical microscopy (POM) with an Axiolab Zeiss optical microscope equipped with a Linkam TP92 hot stage.

X-ray diffraction patterns were recorded at room temperature with a Siemens D5000 diffractometer in the θ - θ configuration, fitted with an Anton Paar TTK temperature chamber. CuK_α radiation was used and graphite was the second monochromator. The Bragg angle step was 0.05° and the time per step 3 s.

3. Experimental results and discussion

3.1 Thermal characterization

In this paper, we prepared hybrid coatings through dual-cure processes involving the photopolymerization of an acrylic resin and the subsequent hydrolysis/condensation of alkoxy silane groups, in the presence of three different liquid crystalline oligomers bearing methacrylic reactive groups, synthesized on purpose.

The LC oligomers, namely LC1, LC2 and LC3, exhibited nematic phase, as inferred from DSC, POM and XRD analyses. Figure 2 presents the first heating DSC scan of LC1, LC2 and LC3. In the case of LC1, DSC analysis combined with POM observation showed a melting endotherm from crystalline to LC phase centered at 80°C , followed by a polymerization exotherm of methacrylic groups starting at about 125°C and centered around 143°C . A second scan performed on the same oligomer after crosslinking revealed a T_g at about 60°C and a broad clearing endotherm at ca. 140°C . As far as LC2 is concerned, the melting from crystalline to the LC phase was observed at 70°C , while crosslinking started at 100°C ; the T_g of the crosslinked oligomer was about 63°C and its clearing around 130°C . Finally, LC3 sample was a liquid crystalline paste, which became isotropic at 84°C and started to crosslink at about 110°C ; the crosslinked oligomer showed a T_g at 61°C and a broad clearing endotherm centered around 127°C . From the above considerations, we

chose to perform the sol-gel process at 75°C, which is lower than the crosslinking temperature of the as-synthesized LC oligomers, thus preventing their crosslinking during the dual-cure process. In addition, the adopted conditions for the sol-gel process (4 hours at 75°C) have already led to high degree of condensation on the same UV-curable systems without LC oligomers [47].

Table 2 collects the results obtained from DSC experiments. It is noteworthy that the T_g values, and therefore the crosslinking density of the cured polymer networks, obtained without MEMO and TEOS (i.e. the inorganic phase precursors) seem to be independent from the type of LC oligomer present in the UV-curable mixture: indeed, LC1S1, LC2S1 and LC3S1 show almost the same T_g value, around -39°C. This finding suggests that the presence of any LC unit does not affect the packing of the macromolecular chains upon photo-polymerization. Furthermore, the data reported in Table 2 clearly indicate that the formation of the silica phase hinders the mobility of the polymeric chains since the T_g values significantly increase on increasing TEOS concentration (and therefore the resulting silica content).

All the samples have been characterized by XRD at room temperature coupled with POM in order to assess their LC character. These findings will be further described in the next paragraph. As far as the stability of the LC phase is considered, by diluting the LC phase into BEMA, a strong decrease of the clearing points is observed, as expected (see samples LC1S1, LC2S1 and LC3S1).

The stability range of the LC phase can be roughly estimated as the difference between T_c and T_g : more specifically, the presence of the silica phase lowers the stability of the LC counterpart as a consequence of the decrease of $T_c - T_g$. At the same time, the clearing enthalpies (ΔH_c) show a slight increase when the LC units are embedded into the cured systems.

3.2 Morphological characterization

Several characterization techniques have been exploited for thoroughly assessing the morphology of the obtained coatings: in particular, POM, XRD, SEM, ESEM and AFM analyses have been used for this purpose. XRD patterns (some of them are plotted in Figure 3) show a broad halo centered

around $2\theta=20^\circ$, which, combined with a strong birefringence observed by POM, indicate the existence of nematic phase, homogeneously distributed within the UV-cured network.

In addition, only in the presence of the highest amounts of TEOS (samples LCXS4), LC moieties tend to segregate: as an example, Figure 4 clearly shows this phenomenon concerning LC2S4 sample (segregated, Figure 4c) as compared to LC1S2 and LC2S3 (both not segregated, Figures 4a and b, respectively).

Figure 5 plots some typical SEM pictures referring to the morphologies of the cross sections fractured in liquid nitrogen for LC3S1 (Figure 5a), LC3S2 (Figure 5b), LC3S3 (Figure 5c) and LC3S4 (Figure 5d). A similar behaviour was observed for all the coatings investigated. It is worthy to note that the fractured surface significantly changes, showing an increased roughness due to the presence of increasing amounts of silica phases, irrespective of the segregation phenomena of the LC phases, which were observed in the case of LCXS4 samples.

Aiming to further complete the morphological characterization, AFM measurements have been carried out on both the sides of the coatings investigated. A typical AFM picture referring to the LC1S1 “gas” side (i.e. the side exposed to UV-radiation) is presented in Figure 6a (as bi-dimensional topographic image). It is noteworthy that the LC phase is homogeneously distributed within the UV-cured network, thus further confirming the findings already described in POM observations. In the presence of silica-forming precursors (i.e. MEMO and TEOS, sample LC1S3, Figure 6b), the formation of conical silica shapes occurs, thus indicating that the presence of LC units is responsible for the growing of silica nanoneedles. This topology was not observed in the absence of LC phases, as already reported in the literature [44]: thus we can hypothesize the occurrence of an interaction between LC units and the inorganic precursors during the sol-gel process, so that silica is constrained to grow in an acicular morphology.

The same AFM measurements have been also carried out on the glass side of the films (i.e. the surface in contact with the glass substrate, which the UV-curable mixtures have been coated on).

Figure 6c depicts the typical morphology observed. It is noteworthy that the acicular silica growing

is much less pronounced with respect to the gas side of the coatings, probably because of the presence of the glass substrate, which is rigid and seems to limit the growing of the silica nanoneedles. As a matter of fact, EDX analyses performed on both the sides of the coatings have clearly shown an asymmetric distribution of the silica phase: as an example, for LC1S3 sample, the bulk theoretical silica content, on the basis of its composition, is around 5.5 wt.%; on the glass side, this content decreases up to ca. 3.1 wt.%, while on the gas side of the film, it is around 4.6 wt.% (these values are an average of at least 6 measurements).

Aiming to further clarify the topology of the hybrid coatings, ESEM measurements have been performed on their cross-section (fractured in liquid nitrogen). **Figure 7** shows a typical picture referring to LC1S3 sample. A significant anisotropy can be observed: indeed, two different regions of crack propagation can be distinguished. The former, close to the “gas side” of the coating, shows the crack propagation lines, which are perpendicularly oriented to the surface of the coating; on the contrary, the cross-section region close to the glass side reveals isotropic crack propagation, with a smooth fracture surface. These findings have been further confirmed through AFM analyses performed on the same cross-sections: as depicted in **Figures 8a, b and c** for LC1S3, moving from the glass side to the gas one, a remarkable change in the samples topography is observed.

4. Conclusion

A dual-cure process has been exploited for obtaining hybrid organic-inorganic coatings containing reactive LC units synthesized on purpose. All the samples exhibited nematic liquid crystalline phase. SEM and ESEM microscopy measurements, together with AFM and POM observations have clearly shown that the morphology of the coatings is strictly related to the composition of the hybrid films and to the presence of LC units. Furthermore, the distribution of silica on the two sides of the films is asymmetric and tends to form conical shapes preferably on the “gas side” of the hybrid coatings, as clearly assessed by atomic force microscopy measurements. Finally, the presence of the inorganic silica domains is able to limit the mobility of the polymer chains, increasing the T_g of the

polymer network, and to somehow contribute to the occurrence of segregation phenomena of the LC phase.

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Figure Captions

Fig. 1: Chemical structure of BEMA, MEMO, photoinitiator and of LC1 oligomer.

Fig. 2: DSC thermograms (first heating scan) of (a) LC1, (b) LC2, (c) LC3 oligomers.

Fig. 3: XRD patterns of some hybrid films: (a) LC1S3; (b) LC2S2; (c) LC3S2; (d) LC2S1; (e) LC1S1; (f) LC1S4; (g) LC1S2.

Fig. 4: Optical micrographs between crossed polars at room temperature of LC1S2 (a), LC2S3 (b) and LC2S4 (c).

Fig. 5: SEM pictures of cross-section morphologies of LC3S1 (a), LC3S2 (b), LC3S3 (c), LC3S4 (d).

Fig. 6: AFM topography images of samples (a) LC1S1 (“gas” side) and (b, c) LC1S3 on the (b) “gas” and (c) “glass” sides.

Fig. 7: ESEM picture of LC1S3 cross-section.

Fig. 8: AFM topography images of LC1S3 sample: (a) cross-section close to the “glass” side, (b) cross-section, in between “glass” and “gas” side, (c) cross-section, close to the “gas” side.

Table 1: Composition of the UV-curable mixtures

Sample	BEMA (wt.%)	MEMO (wt.%)	TEOS (wt.%)	LC (oligomer wt.%)
1	94.0	0	0	6.0
2	75.2	18.8	0	6.0
3	51.2	12.8	30.0	6.0
4	35.2	8.8	50.0	6.0

Table 2: Thermal properties of LC oligomers and cured systems.

Sample	T _g (°C)	T _c (°C) ^a	T _c -T _g (°C)	ΔH _c (J/g)	Segregation ^b
LC1 ^c	60	140	80	8.8	-
LC2 ^c	63	130	67	5.9	-
LC3 ^c	61	127	66	5.5	-
LC1S1	-38	102	140	12.8	No
LC1S2	-32	85	117	8.3	No
LC1S3	-31	81	112	16.4	No
LC1S4	-30	83	113	17.9	Yes
LC2S1	-39	102	141	17.2	No
LC2S2	-46	89	135	16.4	No
LC2S3	-36	94	130	20.9	No
LC2S4	-32	63	95	26.5	Yes
LC3S1	-40	87	127	25.9	No
LC3S2	-34	84	118	15.6	No
LC3S3	-28	95	123	19.7	No
LC3S4	-26	70	96	14.4	Yes

^a Clearing temperature.^b As assessed by POM.^c From DSC 2nd heating scan.

Figure 1
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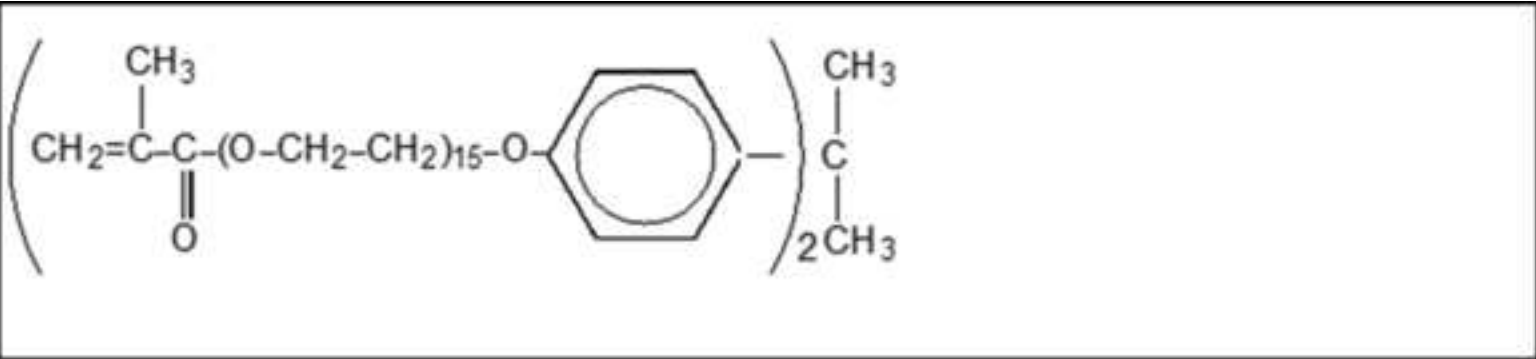
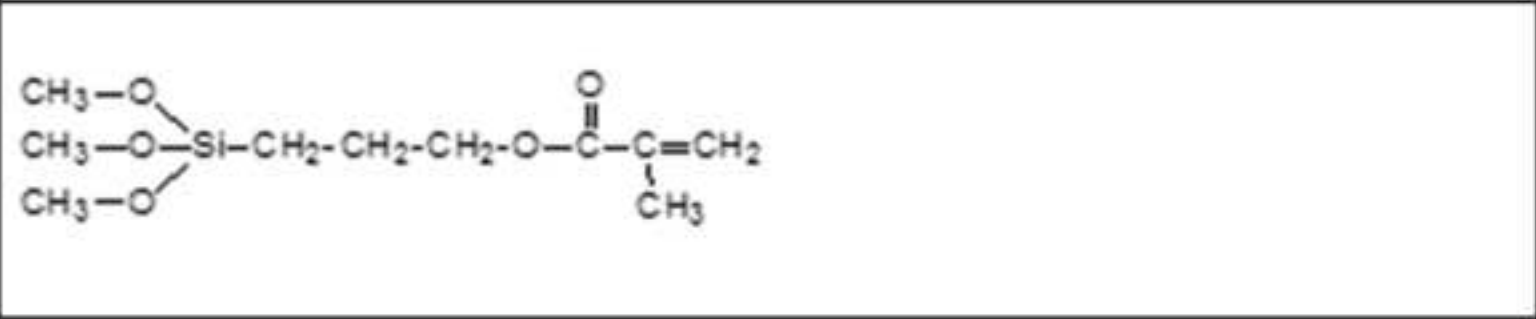
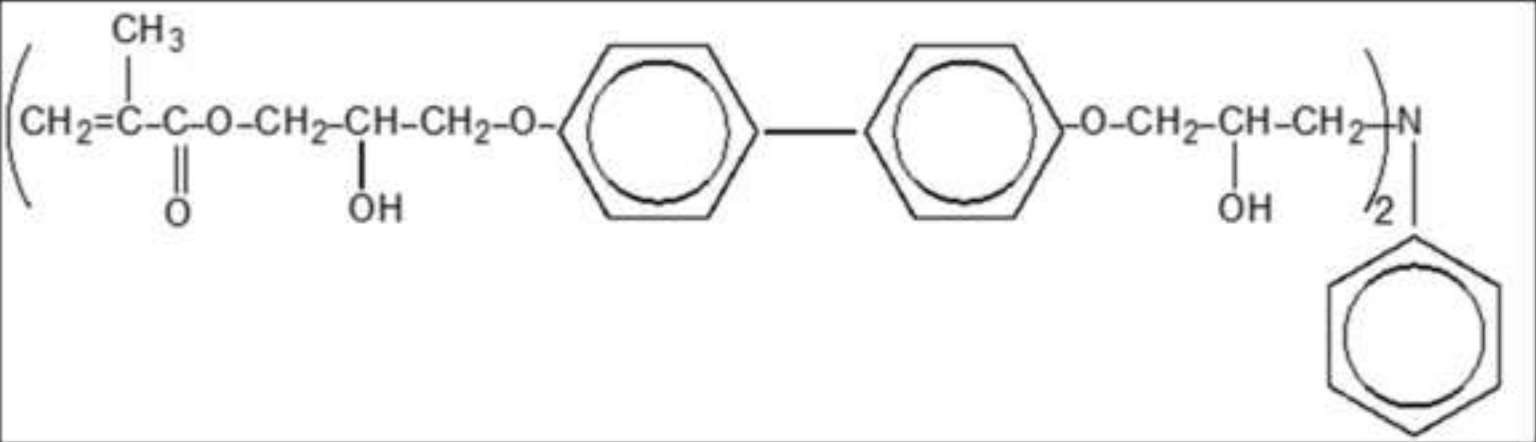
 <chem>CC(C)(C)c1cc(C(=O)OCCc2cc(C)cc(C)c2)c(C)c1</chem>	BEMA
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 <chem>CC(C)(C)C(=O)c1ccccc1</chem>	DAROCUR 1173
 <chem>CC(C)(O)COc1ccc(cc1)-c2ccc(cc2)COCC(C)(C)O</chem>	LC1

Figure 2
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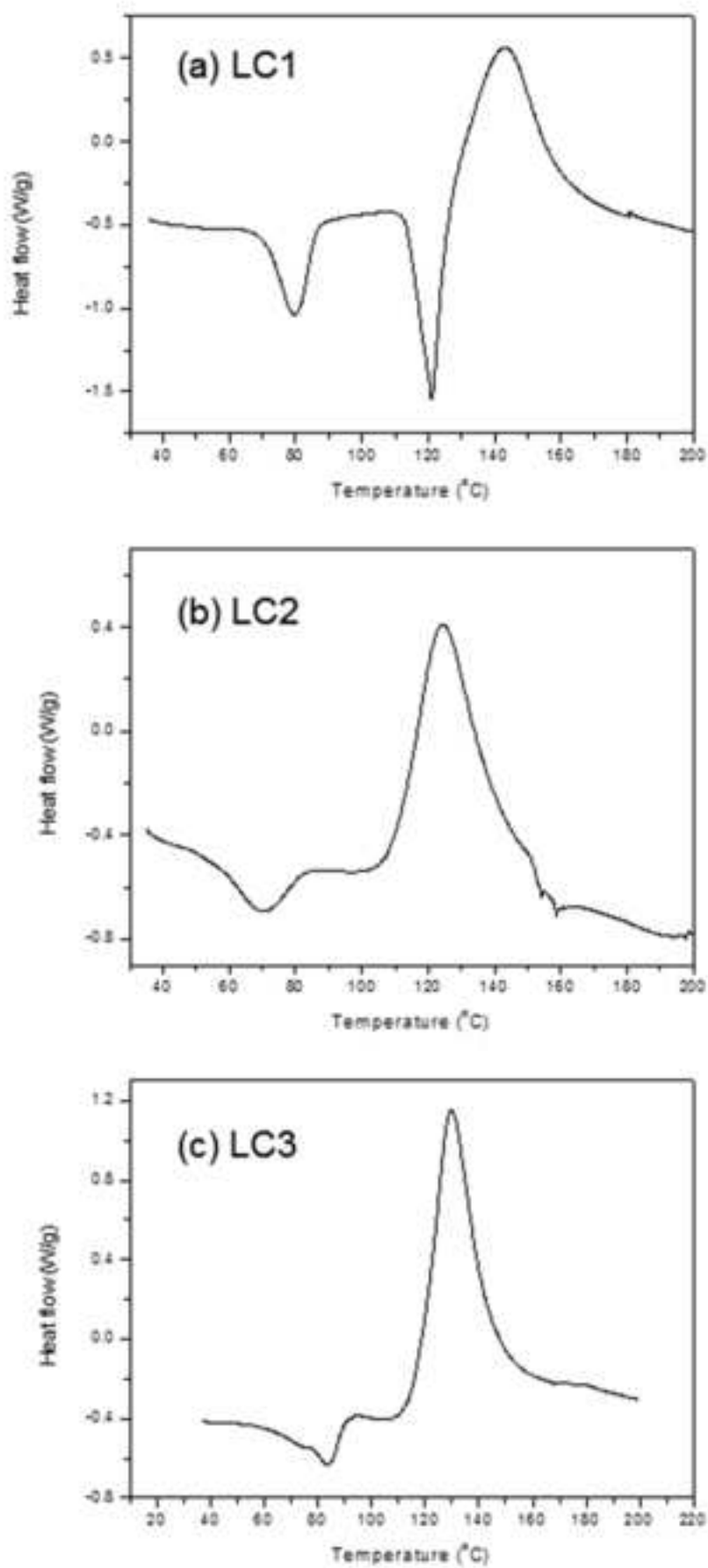


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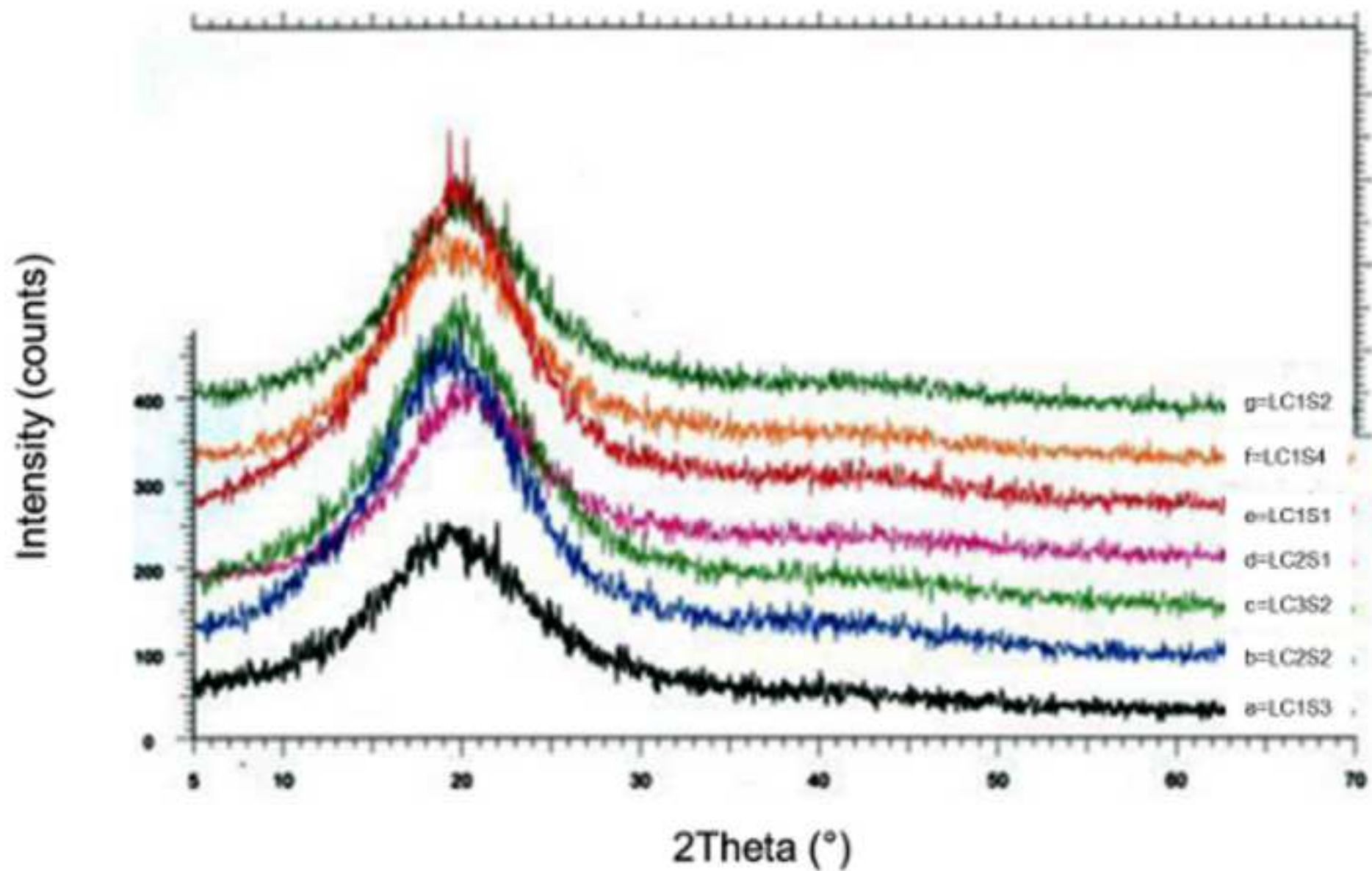


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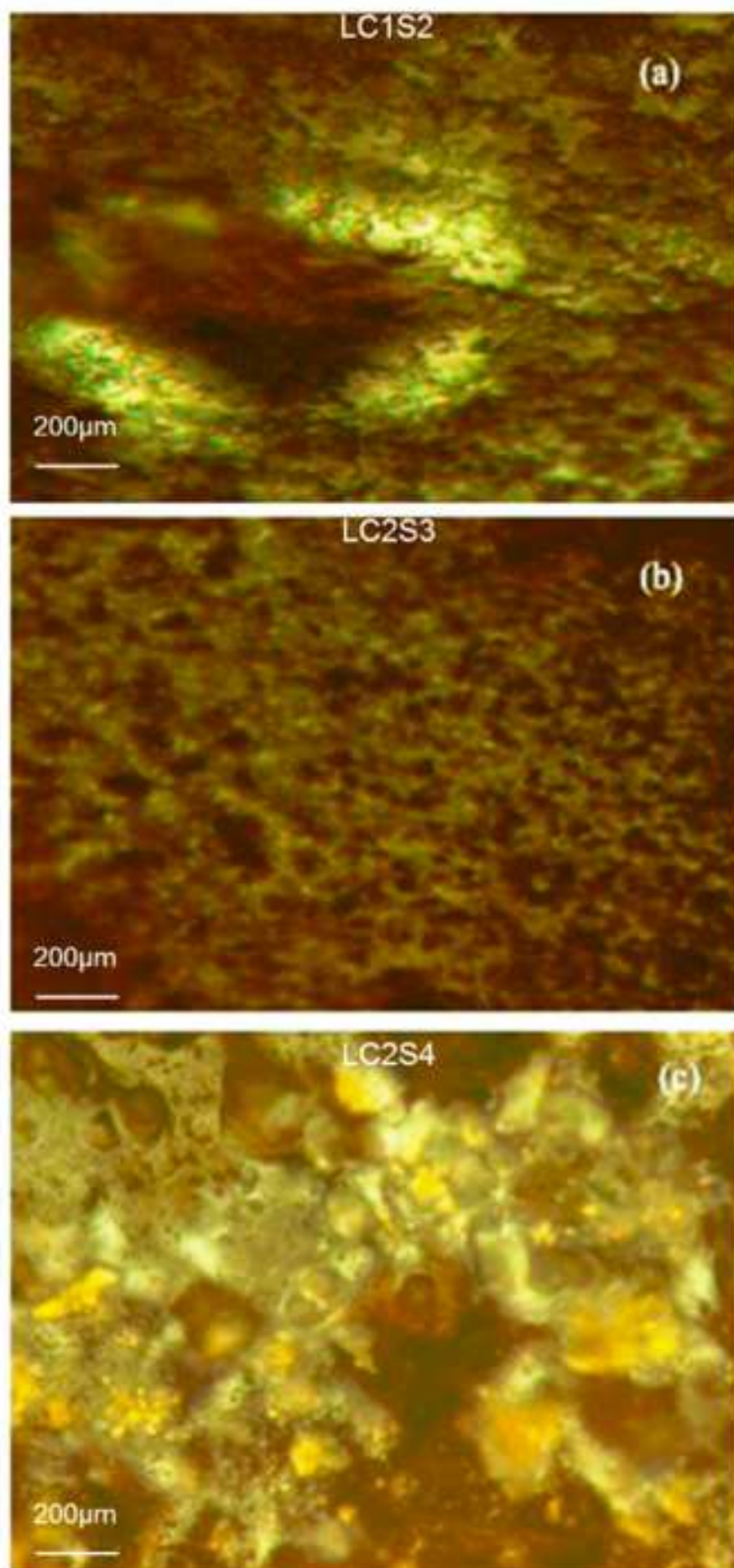


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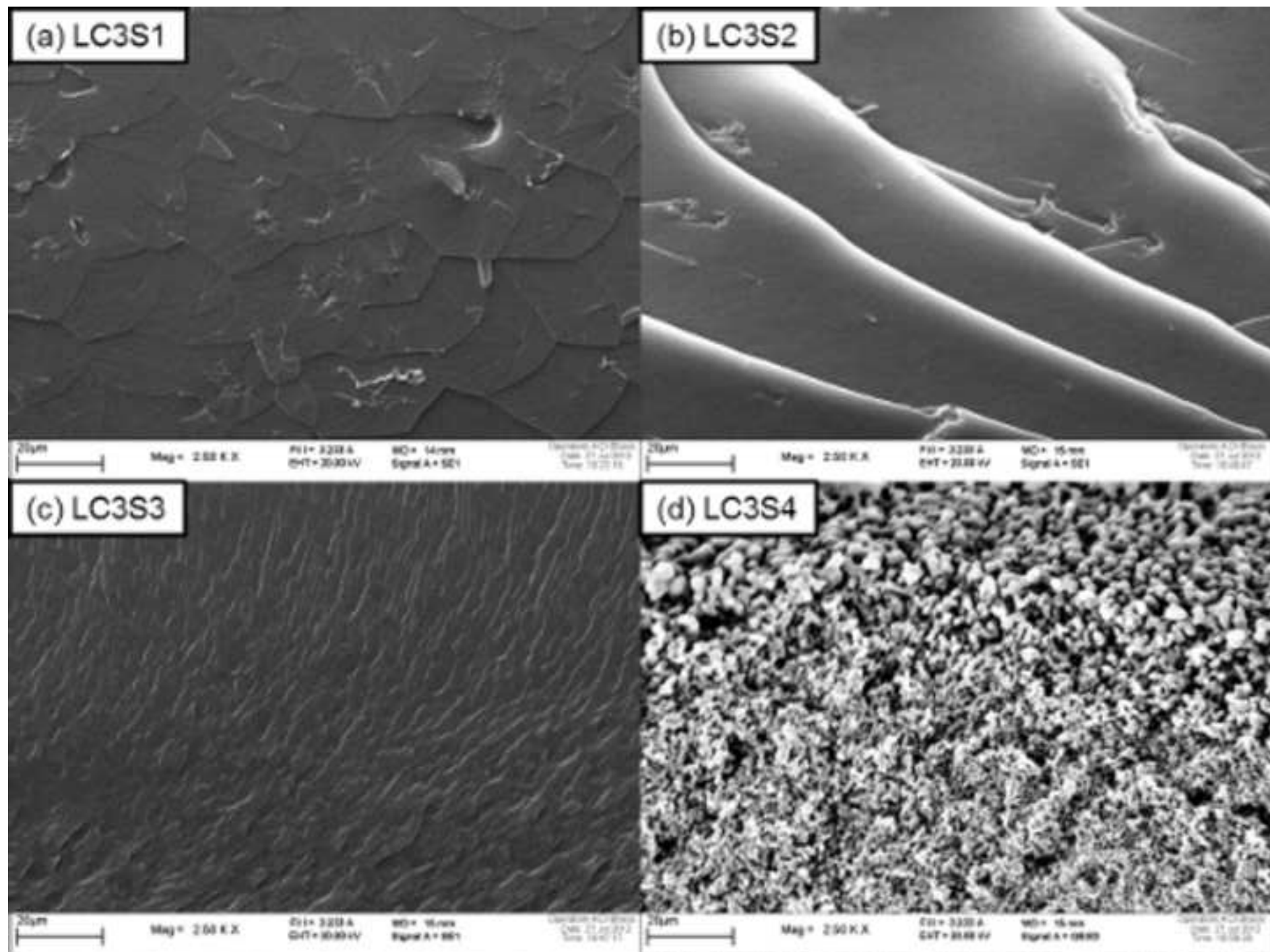


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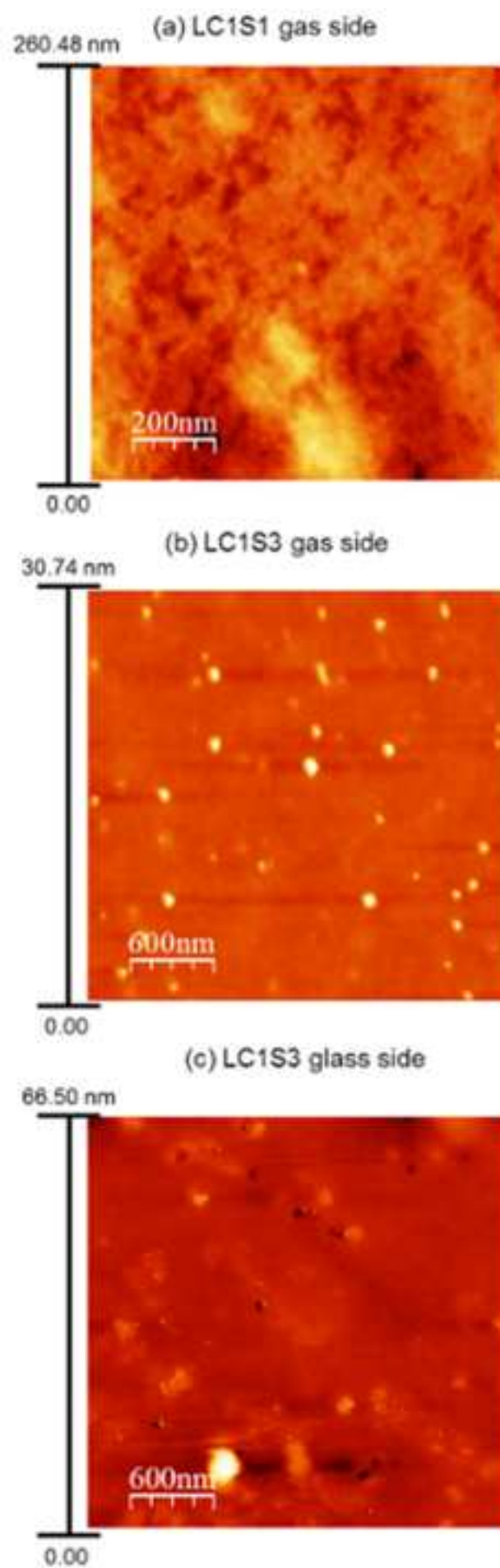


Figure 7
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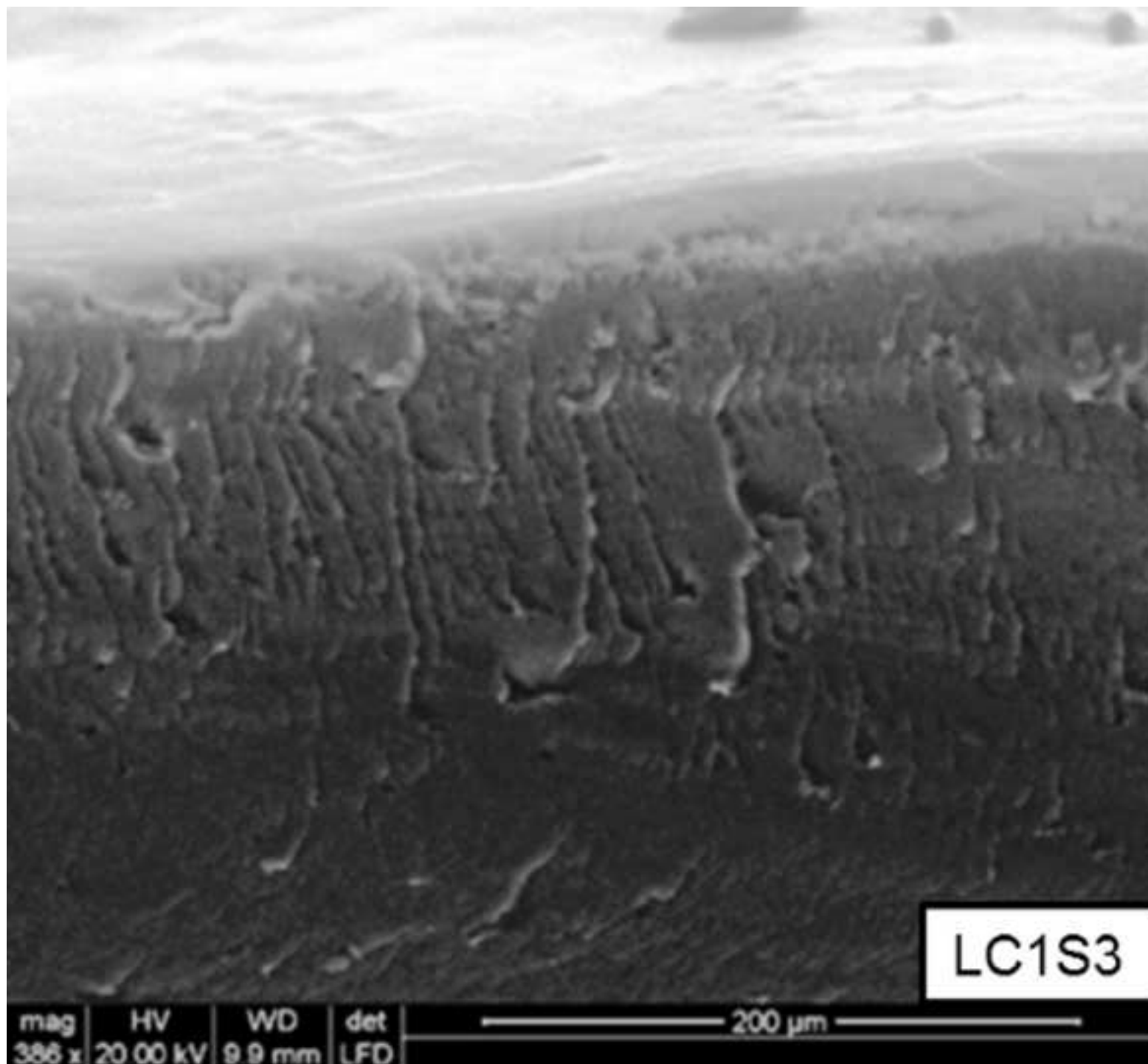


Figure 8

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