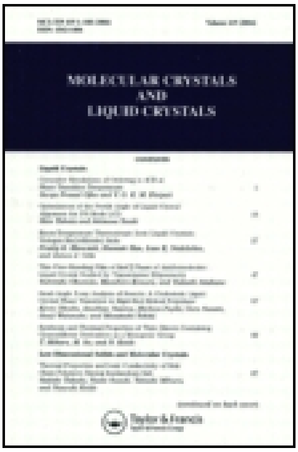

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Kinetics and Molecular Weight Characterization of Poly (2-Ethylhexyl Acrylate) and Liquid Crystal (5CB) Composites

A. Elqidrea [a], R. Meziane [a] & U. Maschke [a]

[a] Unité Matériaux et Transformations (UMET), Université de Lille 1 - Sciences et Technologies, Villeneuve d'Ascq Cedex, France

To cite this article: A. Elqidrea, R. Meziane & U. Maschke (2011): Kinetics and Molecular Weight Characterization of Poly (2-Ethylhexyl Acrylate) and Liquid Crystal (5CB) Composites, Molecular Crystals and Liquid Crystals, 547:1, 128/[1818]-134/[1824]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.572804

Mol. Cryst. Liq. Cryst., Vol. 547: pp. 128/[1818]–134/[1824], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.572804

Kinetics and Molecular Weight Characterization of Poly (2-Ethylhexyl Acrylate) and Liquid Crystal (5CB) Composites

A. ELQIDREA, R. MEZIANE, AND U. MASCHKE

Unité Matériaux et Transformations (UMET), Université de Lille 1 –
Sciences et Technologies, Villeneuve d'Ascq Cedex, France

The effect of initiator and liquid crystal 4-cyano-4′-n-pentylbiphenyl (5CB) concentrations on the monomer conversion and molecular weight distributions of the polymer in the free-radical polymerization of 2-ethylhexylacrylate (2-EHA) has been studied and characterized using Fourier transform infrared spectroscopy, differential scanning calorimetry, and gel permeation chromatography. A slight effect of the concentration of the photoinitiator has been observed both on the monomer conversion and the molecular weight distribution of poly (2-EHA). Increasing the amount of 5CB in the initial mixture leads to a decrease of conversion, glass transition temperature of the polymer, molar mass of polymer and of the polydispersity.

Keywords Chain transfer; liquid crystal; molecular weight distribution; polymer; radical polymerization; UV curing

1. Introduction

Radical polymerization has been used for decades to polymerize wide range of monomers and to elaborate polymer dispersed liquid crystals (PDLC).

Poly (2-ethylhexyl acrylate) (PEHA) is used in several applications [1,2], including pressure-sensitive adhesives, coatings, textiles, copolymers and adhesion to various substrates because of its low glass transition temperature and durability. Recently, there is growing interest to develop new methodologies that allow the control of the final structure and the polymer architecture of this polymer.

Photopolymerization has been widely used to produce polymer/liquid crystal composite films with specific structures and physical properties. Photopolymerization entails the use of radiation such as ultraviolet (UV) or tunable laser light sources to polymerize photoreactive monomers. The main advantages of photopolymerization are fast curing speed, uniformity, and ease of controlling the reaction. Polymerization temperature can be low; therefore, the loss of volatile ingredients and degradation of polymer can be avoided considerably [3]. In addition, the

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Address correspondence to U. Maschke, Unité Matériaux et Transformations (UMET), UMR 8207–CNRS, Université de Lille 1 – Sciences et Technologies, Bâtiment C6, 59655 Villeneuve d'Ascq Cedex, France. Tel.: 00 33-3 20 33 63 81; Fax: 00 33-3 20 43 43 45; E-mail: ulrich.maschke@univ-lille1.fr

photopolymerization process is solvent-free and clean, and thus it has diverse applications in the areas of polymer thin films, coatings, adhesives, composites, and advanced optical devices such as flat panel displays, optical switches, and photo-imaging plates [4].

In this work, we focus on the case of poly(2-ethylhexyl acrylate) in short PEHA and the LC 4-cyano-4′-n-pentylbiphenyl (5CB), and study the monomer conversion at different (5CB) concentrations, on one hand, and the effect of changing the UV dose on the molar mass of polymer, on the other hand. The maximum UV dose required to achieve the highest monomer conversion can be determined by FTIR spectroscopy. The infrared measurement has the advantage of conducting a series of measurements without affecting the produced polymer, which enables us to follow the actual evolution of the monomer during polymerization [5,6].

By measuring the intensity of the double bond of the acrylate groups before and after the polymerization, we can calculate the conversion rate of the monomer. The disappearance of the peak by applying UV dose can be used to evaluate quantitatively the monomer conversion.

The initial mixture consists of a monofunctional monomer (2-EHA), 5CB and a small amount of photoinitiator (Darocur 1173), added to initiate the photopolymerization process. The concentration of monomer in the monomer/LC mixture was varied from 100 wt% (pure monomer) to 30 wt% to cover nearly the whole range of composition.

2. Experimental Methods

2.1. *Materials*

The monomer 2-ethylhexyl acrylate (EHA) and the polymer poly(2-ethylhexyl acrylate) (PEHA) were supplied by Sigma-Aldrich. The LC 4-cyano-4′-n-pentylbiphenyl (5CB) was purchased from Merck Eurolab GmbH (Darmstadt, Germany) and was characterized by the transition temperatures $T_{CN} = 23°C$ (crystalline-nematic) and $T_{NI} = 35.3°C$ (nematic-isotropic).

2.2. *Sample Preparation*

Mixtures of EHA and 5CB were prepared with different LC concentrations and stirred mechanically until they became homogeneous. A drop of the reactive mixture was placed on a NaCl crystal and rolled to a uniform thickness using a wire rod, and then the sample is covered with a flat PET film. This slide is then fixed in a tray and then exposed to UV beam using an irradiation device (Minicure MC4-300 from Primarc UV Technology). The amount of UV dose on the sample is adjusted by controlling the speed of the conveyor belt of the UV device.

The polymerization process was induced by a photoinitiator (Darocur1173 from Ciba, Rueil Malmaison, France) using concentrations between 0.5 to 6 wt%, with respect to the amount of monomer.

2.3. *GPC Measurements*

The samples have been prepared by dissolving 30 mg of PEHA/5CB composites in 10 ml of THF. The measurement of the molar masses by GPC was performed at

$T = 25°C$ using a Waters apparatus including a Waters 515 pump, a Waters 717 plus autosampler, a differential refractometer Waters 410, and Stryragel columns HR3 and HR 3E (5 μm particles). Each experiment elapsed nearly 1 hour with a flow rate of 1 mL/min [7].

The different peaks obtained from the GPC measurements appear as a function of the retention time of the components, the molar mass of each polymer sample has been determined using the polynomial of the calibration curve.

3. Results and Discussion

Photopolymerization kinetics and molecular weights of polymer/LC samples are presented and discussed as a function of UV curing conditions, i.e., concentration of photoinitiator, UV exposure time and concentration of LC 5CB. Furthermore, the variation of the polymer molar mass with the LC concentration in the precursor mixture after polymerization is reported using GPC.

3.1. *Conversion Rate with the Initiator Concentration*

The dependence of the monomer conversion of photopolymerization on the concentration of the photoinitiator system for the 2-EHA monomer mixture was studied in order to determine the influence of the photoinitiator on the conversion and the molecular weight distribution of the polymer.

The results are shown in Figure 1. It is observed that the initial photopolymerization rate is directly proportional to the square root of the photoinitiator concentration, according to the following classical equation:

$$R_p = k_p[M]\sqrt{\left(\frac{f\ k_d[I]}{k_t}\right)}$$

where k_p, k_t and k_d are the propagation and termination rate constants, respectively, [M] is the initial concentration of monomers, f is the mole fraction of initiator

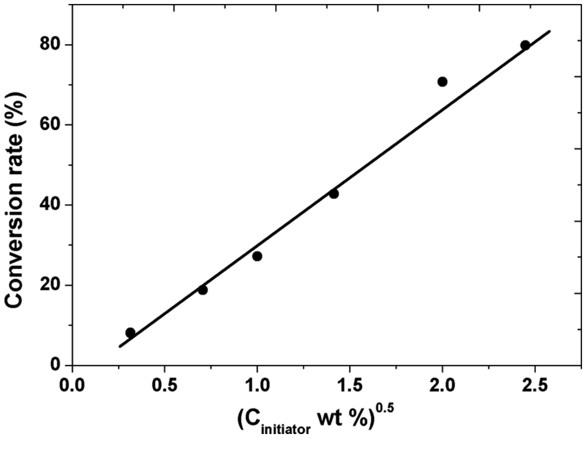

Figure 1. Dependence of the rate of polymerization on the square root of the photoinitiator concentration $C_{initiator}$.

radicals and [I] is the initial initiator concentration. Therefore, the rate of polymerization is dependent on the monomer concentration and the square root of the initiator concentration.

The effect of the concentration of photoinitiator on the kinetic curves is shown in Figure 2. The maximum rate is reached for the shortest time period with the highest photoinitiator concentration. The initial part of the kinetic curves show high conversion rate, doubling the amount of the initiator from 2 to 4% resulted in increasing the conversion of about 35%, whereas further increase from 4 to 6% initiator gave very slight effect on the reaction side. These results show the limitation of the kinetic equation at very high concentration of the photoinitiator.

It is known that the reaction rate and the intensity of irradiation are directly proportional:increasing the intensity of light absorbed by a photoinitiator increases the photopolymerization rate. A quantitative evaluation of the influence of the irradiation dose on the photopolymerization process and the mechanical properties of the obtained polymer is currently in progress.

3.2. *Kinetic Study of Photopolymerization of PEHA/5CB Composites*

To assess the influence of different 5CB concentrations on the photopolymerization process, the radical polymerization under UV irradiation has been studied with several 2-EHA/5CB compositions (30wt-%, 50wt-% and 70wt-% of 5CB). This wide range of 5CB concentrations has been chosen to cover the whole phase diagram.

The kinetic study of photopolymerization of the above composites was carried out under normalized experimental conditions and the kinetic curves are shown in Figure 3.

The time required to reach maximum conversion is low for pure monomer compared to monomer/LC composite mixtures. At low 5CB concentration, a higher conversion rate is observed at the beginning of the reaction compared with the pure monomer, this occurs as a result of the dilution effect since 5CB acts as a solvent to

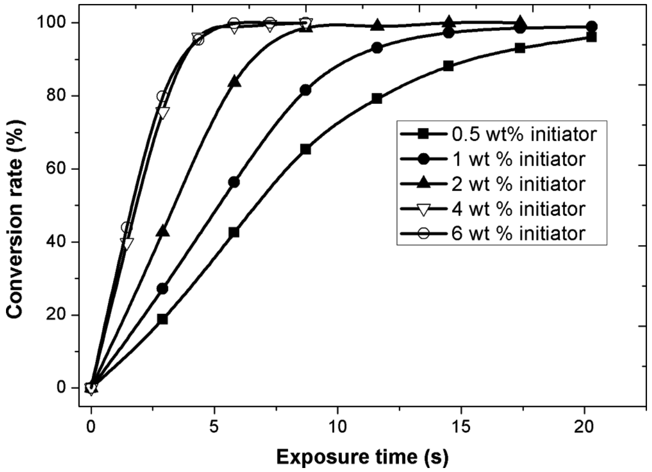

Figure 2. The effect of the photoinitiator concentration on the photopolymerization of 2-EHA. UV irradiation intensity = 120 mJ/cm^2 per passage.

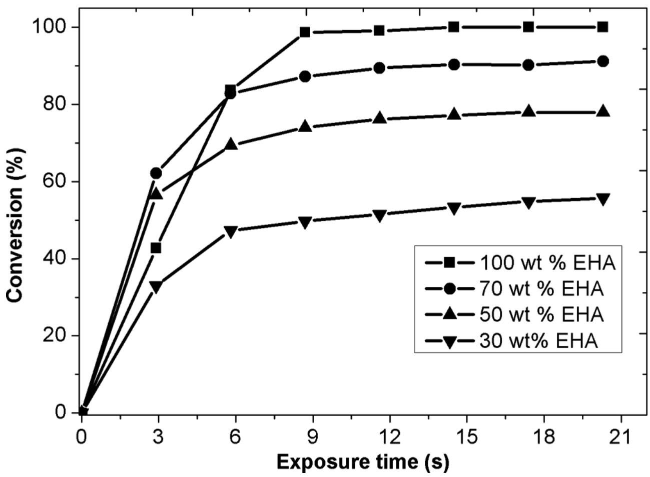

Figure 3. Kinetic curves of the photopolymerization of 2-EHA/5CB composites at 2% initiator. The UV irradiation intensity = 120 mJ/cm^2 per passage.

the monomer enhancing to some extent the molecular interactions between monomer molecules.

All composites show similar behavior under irradiation; an initial relatively high polymerization rate was observed, followed by a clear decrease in their polymerization activity at a certain level of conversion, apparently resulting from the slow movement of the monomer towards the polymer chain.

3.3. *Variation of the Polymer Molar Mass with LC Concentration in PEHA/5CB Systems*

A series of samples with a monomer concentration ranging from 100 wt% (no LC) to 30 wt% (70 wt% LC in the monomer/LC mixture) were exposed to the UV light. The obtained polymer/LC films were analyzed by GPC measurements.

We could measure the variation of the polymer molar mass in terms of the LC concentration using GPC as shown in Figure 4. Weight- and number-averaged molar masses M_w and M_n exhibit a considerable drop when the LC concentration increases. This result means that as the precursor system is more diluted with the addition of LC, the chain growth stop at a smaller mass of the polymer, since the probability of contact between two reacting species decreases.

The M_w and M_n values are averages of two measurements made on samples prepared under the same polymerization conditions. The dashed lines in Figure 4 present M_w and M_n of the commercial PEHA. These values intercept with those of the polymer in the systems in the vicinity of 65 wt% 5CB. Below this concentration, the samples have higher molar masses compared to those of the commercial polymer, it can be realized that at low concentration of reacting monomers the polymerization rate is low, which results in lower molecular weight of polymer.

The inset in Figure 4 shows that for the UV-cured systems the variation of the polydispersity exhibit a trend opposite to those of the molar mass curves. The polydispersity increases remarkably at higher molar masses of the polymers, this agrees with those results obtained in Figure 4 that the presence of 5CB prevents the formation of high molar mass polymer which results in lower polydispersity.

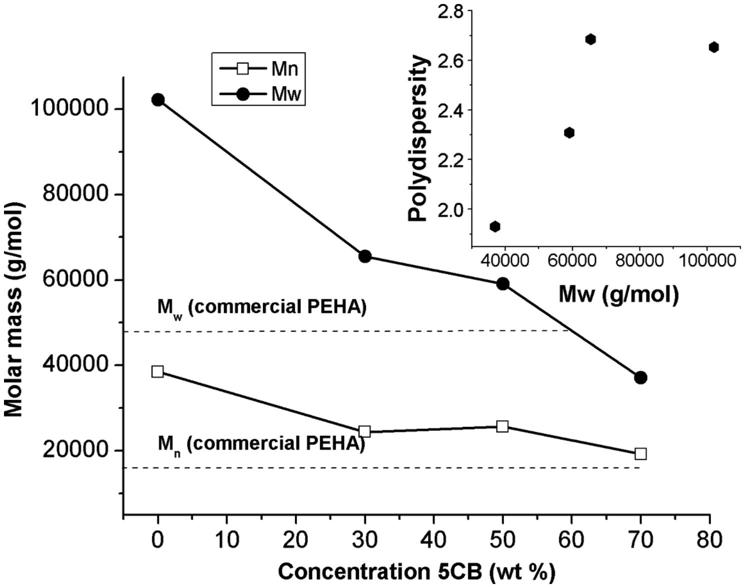

Figure 4. The change of the molar mass of PEHA as a function of 5CB concentration for the PEHA/5CB system under UV curing. Inset: Variation of the polydispersity M_w/M_n with the molar mass of polymer.

4. Conclusions and Perspectives

The rate of photoinitiated polymerization of the monomer mixture obeyed the ideal photopolymerization equation and was proportional to the square root of the concentration of the initiator system. The trend of the conversion rate of the photopolymerization of 2EHA/5CB systems obtained was similar to that of pure monomer mixture but with lower conversion.

The behavior of photopolymerization rate in the composites studied could be explained by considering that the interactions between the monomer and the LC produce a phase separation where a lower molecular mobility cause a decrease in the polymerization rate; on the other hand, at the initial stage of photopolymerizatation the presence of LC direct the monomer molecules toward each others, which cause an increase in the polymerization rate.

Furthermore, the amount of LC dissolved in the polymer has a considerable impact on its thermophysical parameters, which consequently affect the overall properties of the polymer/LC composite material.

The effect of the UV light irradiation intensity on the morphology and the mechanical properties of the polymer/LC materials is currently under investigation.

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