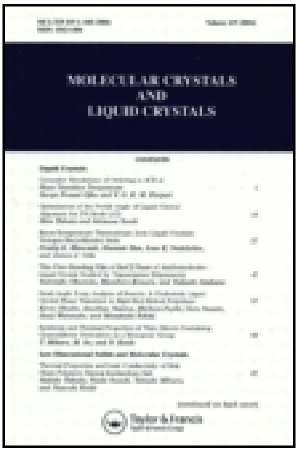
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 11:08
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Liquid Crystallinity of Random Copolymers of Polymethacrylates Containing Biphenyl Moieties Synthesized by Atom Transfer Radical Polymerization

Rei Taguchi [a], Shoichi Kubo [a], Shingo Hadano [b], Tomokazu Iyoda [b] & Masaru Nakagawa [a]

[a] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Japan

[b] Chemical Resources Laboratory, Tokyo Institute of Technology, R1-25, 4259 Nagatsuta, Midori-ku, Yokohama, Japan

Published online: 11 Sep 2013.

To cite this article: Rei Taguchi, Shoichi Kubo, Shingo Hadano, Tomokazu Iyoda & Masaru Nakagawa (2013) Liquid Crystallinity of Random Copolymers of Polymethacrylates Containing Biphenyl Moieties Synthesized by Atom Transfer Radical Polymerization, Molecular Crystals and Liquid Crystals, 579:1, 30-33, DOI: 10.1080/15421406.2013.805049

To link to this article: http://dx.doi.org/10.1080/15421406.2013.805049

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Mol. Cryst. Liq. Cryst., Vol. 579: pp. 30–33, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.805049

Liquid Crystallinity of Random Copolymers of Polymethacrylates Containing Biphenyl Moieties Synthesized by Atom Transfer Radical Polymerization

REI TAGUCHI,[1] SHOICHI KUBO,[1,*] SHINGO HADANO,[2]
TOMOKAZU IYODA,[2] AND MASARU NAKAGAWA[1]

[1]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Japan
[2]Chemical Resources Laboratory, Tokyo Institute of Technology, R1-25, 4259 Nagatsuta, Midori-ku, Yokohama, Japan

*4-(4′-Cyanobiphenyloxy)butyl methacrylate, MA(4OCB), was copolymerized with 8-(4′-hexyloxybiphenyloxy)octyl methacrylate, MA(8O6RB), or butyl methacrylate, MA(Bu), by atom transfer radical polymerization. Phase transition behaviors and liquid crystalline properties of the random copolymers with small polydispersity were compared with those of respective homopolymers. The thermal analysis suggested that both biphenyl mesogens in the p[MA(4OCB)-*co*-(8O6RB)] random copolymers were oriented together rather than segregated. In the case of the p[MA(4OCB)-*co*-MA(Bu)] random copolymers, the butyl side-chains worked to diminish liquid crystallinity by disturbing orientation of the biphenyl mesogen due to thermal fluctuation.*

Keywords atom transfer radical polymerization (ATRP); biphenyl mesogen; polymer liquid crystal; random copolymer

Introduction

Side-chain liquid crystalline polymers (SLCPs) have attracted much interest due to their ability to form oriented structures leading to optical application [1,2]. The thermal behaviors and liquid crystalline properties are mainly dominated by the chemical structures of the side-chain mesogen and spacer, as well as the main-chain backbone. Up to date, many kinds of SLCPs have been synthesized to obtain targeted properties suitable for various functions. Another approach to adjust the liquid crystalline properties is to copolymerize monomers to introduce a different side-chain. The latter strategy should give a facile way to tune a desired property by using a known mesogen. Although there are several reports on side-chain liquid crystalline random copolymers [3–6], the polymers with large polydispersity are synthesized by conventional free-radical polymerization. Because the polydispersity of SLCPs affects their liquid crystalline properties [7,8], it is difficult to investigate the true effect of introducing randomly different side-chain mesogens on the liquid crystallinity by removing the influence of polydispersity. Atom transfer radical

---

[*]Address correspondence to Shoichi Kubo. Tel.: +81-22-217-5672; Fax: +81-22-217-5671. E-mail: skubo@tagen.tohoku.ac.jp

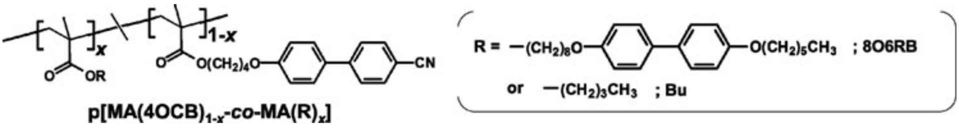


Figure 1. Chemical structures of random copolymers synthesized by ATRP in this study.

polymerization (ATRP) was developed as one of living radical polymerization methods to synthesize polymers with small polydispersities [9–11]. Here, we synthesized side-chain liquid crystalline random copolymers with small polydispersity using methacrylates containing cyanobiphenyl, hexyloxybiphenyloxy, and butyl moieties by ATRP. The phase transition behaviors and liquid crystalline properties were compared with those of respective homopolymers.

Experimental

p[MA(4OCB)-*co*-MA(8O6RB)] and p[MA(4OCB)-*co*-MA(Bu)] random copolymers with various monomer ratios and pMA(4OCB), pMA(8O6RB), and pMA(Bu) homopolymers were synthesized by ATRP, and the chemical structures are shown in Figure 1. A simple methacrylate monomer or binary methacrylate monomers (1.0 mmol), ethyl 2-bromoisobutyrate (10 μmol), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (30 μmol) were dissolved in 2.0 mL of anisole. The solution was put into a 10 mL schlenk tube and degassed through three cycles of vacuum and replace with Ar, and added to Cu(I)Cl (30 μmol). The mixture was stirred at room temperature for 10 min and at 80°C for 24 h under an Ar atmosphere. The reaction solution was passed through an Al_2O_3 column using chloroform as an eluent. After evaporation, a polymer was redissolved in THF and reprecipitated into methanol twice. The copolymer composition was determined by ^{1}H-NMR analysis. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were measured by gel permeation chromatography (GPC) calibrated with polystyrene standards. The thermal property was characterized using a differential scanning calorimeter (DSC) and a polarized optical microscope (POM).

Results and Discussion

Table 1 lists feed mole fractions of respective methacrylate monomers and characterizations of the random copolymers and homopolymers prepared by ATRP. Most of the polymers except for p[MA(4OCB)-*co*-(8O6RB)] at $x = 0.18$ (sample **2**) showed a polydispersity smaller than 1.19. We successfully controlled the polydispersity by ATRP.

Figure 2 shows the DSC thermograms on the second heating processes and POM images of p[MA(4OCB)-*co*-MA(8O6RB)] (sample **1**–**4**) and p[MA(4OCB)-*co*-MA(Bu)] (sample **1**, **5**–**8**). Each phase transition enthalpy (ΔH/kJ mol^{-1}) from a liquid crystal phase to an isotropic phase is also shown near the DSC curve. A parenthesized value near the actual enthalpy means the calculated ΔH_{expect} value under the assumption that the binary mesogens independently oriented and caused the phase transition. The calculation was based on the following equation.

$$\Delta H_{\text{expect}} = (1 - x)\Delta H_{\text{pMA(4OCB)}} + x\Delta H_{\text{pMA(R)}}$$

Table 1. Characterizations of the copolymers and homopolymers prepared by ATRP

Sample	R	Feed mole fraction		Obtained R mole fraction*1	M_n [g mol^{-1}]*2	M_w/M_n*2
		4OCB	R			
1	—	1	0	0	29,300	1.14
2	8O6RB	0.7	0.3	0.18	23,400	1.24
3	8O6RB	0.5	0.5	0.45	33,700	1.19
4	8O6RB	0	1	1	43,500	1.14
5	Bu	0.9	0.1	0.07	20,200	1.13
6	Bu	0.7	0.3	0.18	21,000	1.16
7	Bu	0.5	0.5	0.50	30,600	1.15
8	Bu	0	1	1	16,700	1.14

*1 Determined by ^{1}H NMR *2 Determined by GPC with RI detector

Typical focal conic-fan shaped textures were observed for pMA(8O6RB) by POM at 125°C. This suggested that the phase transition from a smectic phase to an isotropic phase occurred at 148°C with $\Delta H = 7.1$ kJ mol^{-1}. Similarly, the focal conic-fan textures [12] observed at 100°C indicated that pMA(4OCB) brought about a smectic → isotropic phase transition at 108°C with $\Delta H = 1.1$ kJ mol^{-1}. In the case of p[MA(4OCB)-*co*-MA(8O6RB)] at $x = 0.45$, the smectic → isotropic phase transition occurred at 145°C close to 148°C observed for pMA(8O6RB). The observed value of $\Delta H = 4.8$ kJ mol^{-1} was significantly larger than the calculated value of $\Delta H_{\text{expect}} = 3.8$ kJ mol^{-1}. The results supported that the binary biphenyl mesogens were oriented together rather than segregated in the random copolymer, and the phase transition was induced cooperatively. It is probably due to strong π-π stacking between the similar biphenyl mesogens by undulating the main-chains and alkyloxy spacers. In the case of p[MA(4OCB)-*co*-MA(8O6RB)] at $x = 0.18$, the phase transition occurred at 116°C with ΔH of 2.0 kJ mol^{-1}, which was close to $\Delta H_{\text{expect}} = 2.1$ kJ mol^{-1}. This means that the cooperative phase transition was hardly caused and the 8O6RB moiety worked simply as an impurity when the content of the 8O6RB moiety was small.

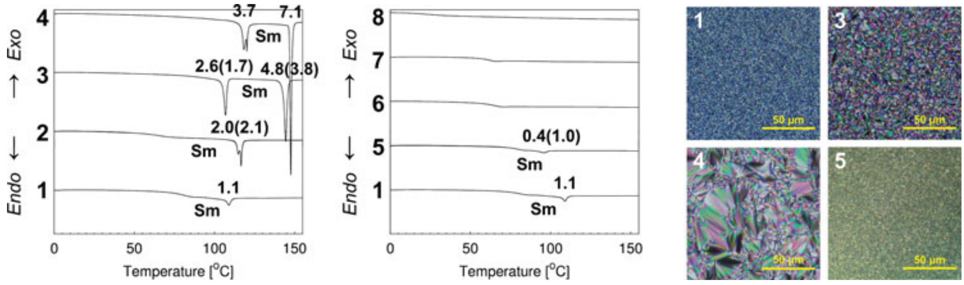


Figure 2. DSC thermograms of pMA(4OCB) **1**, p[MA(4OCB)-*co*-MA(8O6RB)] **2**–**3**, pMA(8O6RB) **4**, p[MA(4OCB)-*co*-MA(Bu)] **5**–**7**, and pMA(Bu) **8** on 2nd heating at a heating rate of 10°C min^{-1}, with POM images of **1** at 100°C, **3** at 130°C, **4** at 125°C, and **5** at 88°C.

The addition of MA(Bu) at $x = 0.07$ to p[MA(4OCB)-*co*-MA(Bu)] decreased a phase transition temperature to 97°C in comparison with 108°C observed for pMA(4OCB). The observed value of $\Delta H = 0.4$ kJ mol^{-1} was smaller than $\Delta H_{\text{expect}} = 1.0$ kJ mol^{-1}. The phase transition derived from a liquid crystal phase disappeared when x was larger than 0.18. A small amount of butyl side-chains could disturb intermolecular interactions among 4OCB moieties.

Conclusions

The random methacrylate copolymers containing 4-(4′-cyanobiphenyloxy)butyl moieties as side-chains were synthesized by ATRP. The thermal analysis in terms of the smectic → isotropic phase transition revealed that the binary biphenyl mesogens cooperatively caused the phase transition without segregation in the case of p[MA(4OCB)-*co*-MA(8O6RB)] with the mole fraction of 8O6RB (x) was 0.45. In contrast, the slight addition of butyl side-chains prevented the 4OCB moieties from inducing liquid crystallinity in the case of p[MA(4OCB)-*co*-MA(Bu)]. The results indicated possibilities that the strategy of random copolymerization by ATRP might attain facile way to tune liquid crystalline properties of polymers.

References

[1] Liu, J.-H., Chou, Y.-L., Balamurugan, R., Tien, K.-H., Chuang, W.-T., & Wu, M.-Z. (2011). *J. Polym. Sci. Pol. Chem.*, *49*, 770.
[2] Shafiee, H., Tagaya, A., & Koike, Y. (2011). *Polym. J.*, *43*, 306.
[3] Craig, A. A., & Imrie, C. T. (1997). *Polymer*, 38, 4951.
[4] Rodekirch, U., Rübner, J., Wolff, D., & Springer, J. (1998). *Macromol. Chem. Phys.*, *199*, 1943.
[5] Craig, A. A., & Imrie, C. T. (1996). *J. Polym. Sci. Pol. Chem.*, *34*, 421.
[6] Isayama, J., Nagano, S., & Seki, T. (2010). *Macromolecules*, *43*, 4105.
[7] Li, M.-H., Keller, P., Grelet, E., & Auroy, P. (2002). *Macromol. Chem. Phys.*, *203*, 619.
[8] Sagane, T., & Lenz, R. W. (1988). *Polymer J.*, *20*, 923.
[9] Wang, J.-S., & Matyjaszewski, K. (1995). *J. Am. Chem. Soc.*, *117*, 5614.
[10] Tian, Y., Watanabe, K., Kong, X., Abe, J., & Iyoda, T. (2002). *Macromolecules*, *35*, 3739.
[11] Ouchi, M., Terashima, T., & Sawamoto, M. (2009). *Chem. Rev.*, *109*, 4963.
[12] Craig, A. A., & Imrie, C. T. (1995). *Macromolecules*, *28*, 3617.