This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 18 February 2013, At: 13:52

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 Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl19

## Phase Transitions of Liquid Crystalline Polyacrylamide

Seiji Ujiie <sup>a</sup> , Kazuhiko Maekawa <sup>a</sup> & Kazuyoshi Iimura <sup>a</sup> <sup>a</sup> Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, Japan Version of record first published: 24 Sep 2006.

To cite this article: Seiji Ujiie, Kazuhiko Maekawa & Kazuyoshi limura (1993): Phase Transitions of Liquid Crystalline Polyacrylamide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 487-490

To link to this article: http://dx.doi.org/10.1080/10587259308030162

#### PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

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.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 487-490 Reprints available directly from the publisher Photocopying permitted by license only © 1993 Gordon and Breach Science Publishers S.A. Printed in the United States of America

# Phase Transitions of Liquid Crystalline Polyacrylamide

SEIJI UJIIE, KAZUHIKO MAEKAWA, and KAZUYOSHI IIMURA

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

(Received December 11, 1992; in final form January 7, 1993)

The liquid crystalline polyacrylamides (PAAD-R) having secondary or tertiary amide groups were synthesized and the thermal properties of PAAD-R were studied. PAAD-H with the secondary amide group exhibited enantiotropically smectic phases with enhanced thermal stability through the formation of hydrogen bonding between amide groups when compared to PAAD-M with the tertiary amide group. Also, a liquid crystalline polyacrylate, which has the same mesogenic side chain as PAAD-H, was prepared and the thermal properties of PAAD-H and PA were compared.

Keywords: liquid crystalline polyacrylamide, secondary amide group, hydrogen bonding, thermal property, smectic

#### INTRODUCTION

In general, organic compounds containing primary or secondary amide groups have much higher melting points when compared to organic ester compounds because of the formation of the hydrogen bonding between amide groups (e.g. phenylbenzoate; mp 69-72°C: benzanilide; mp 164-166°C). In addition, the hydrogen bonding sometimes enables organic molecules to form the liquid crystalline phase.<sup>1,2</sup>

We consider that the introduction of the hydrogen bonding group, just as the secondary amide group, into liquid crystalline polymers is effective for the improvement of thermal properties and liquid crystal formation.

We have synthesized liquid crystalline polyacrylamides (PAAD-R) and polyacrylate (PA) with the same mesogenic side chain as PAAD-R. This paper describes phase transitions of PAAD-R and PA.

#### **RESULTS AND DISCUSSION**

Figure 1 shows the synthetic scheme of monomeric acrylate and acrylamides. The monomers were identified by <sup>1</sup>H NMR measurement. PAAD-R and PA

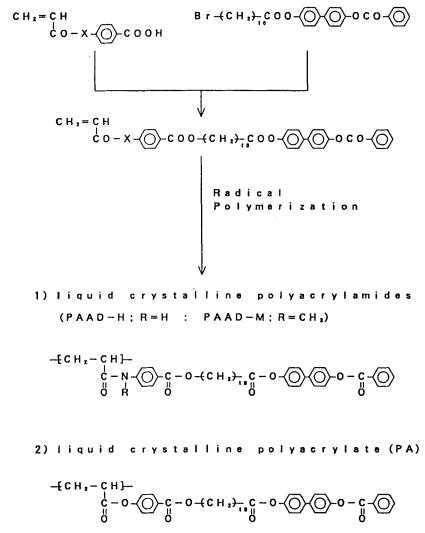


FIGURE 1 Structures of liquid crystalline polyacrylamides and polyacrylate.

were synthesized by radical polymerization of corresponding mesogenic monomers.

In PAAD-R, the mesogenic side chain is attached to the skeletal main chain through the amide linkage group. PA has the structure in which an ester linkage group displaces the amide linkage group in PAAD-R.

The phase transition temperatures were measured with a Mettler DSC 20 and an Olympus polarizing microscope BH-2 equipped with a Mettler hot stage apparatus, and summarized in Table I.

PA and PAAD-R all exhibited two types of enantiotropically ordered smectic phases with mosaic textures in the temperature range of  $T_g$  to  $T_i$  (Table I). The presence of mosaic textures indicates the formation of the ordered smectic phases.<sup>3</sup>

| Phase transition temperatures |             |                      |                      |                      |  |
|-------------------------------|-------------|----------------------|----------------------|----------------------|--|
| Sample                        | <u>™</u> a) | T <sub>g</sub> b)/•C | Ts <sup>c)</sup> /°C | Ti <sup>d)</sup> /°C |  |
| Polyacrylamide                |             |                      |                      |                      |  |
| PAAD-H                        | 6000        | 92.5                 | 157.9                | 209.8                |  |
|                               | 12000       | 94.6                 | 164.3                | 241.1                |  |
| PAAD-M                        | 12800       | 39.0                 | 126.0                | 156.0                |  |
|                               |             |                      |                      |                      |  |
| Polyacrylate                  |             |                      |                      |                      |  |
| PA                            | 6000        | 56.0                 | 121.0                | 143.0                |  |
|                               |             |                      |                      |                      |  |

TABLE I

Phase transition temperatures

62.0

132.0

151.3

b) Glass transition temperature.

18000

- c) Highly-ordered smectic-ordered smectic phase transition temperature.
- d) Ordered smectic-isotropic phase transition temparature.

In the ordered smectic phases, forming in the temperature range of  $T_g$  to  $T_s$  (Table I), a single scattering peak in the wide-angle X-ray region was measured. This demonstrates that the ordered phases with mosaic textures are not solid phases.<sup>4</sup>

PAAD-H containing the secondary amide group showed a higher smectic-isotropic phase transition temperature when compared to PAAD-M containing the tertiary amide group. Also, the smectic-isotropic phase transition temperature  $(T_i)$  of PAAD-H was higher than  $T_i$  of PA. The increase in the thermal stability of PAAD-H is due to the formation of the hydrogen bonding between secondary amide groups.

The effect of temperature on the hydrogen bonding between secondary amide groups was examined by FT-IR measurements.<sup>5</sup> In the smectic phase (100°C and 130°C), the band of the stretching vibration of the amide N-H was measured at 3300 cm<sup>-1</sup>, which indicates the stretching vibration due to the formation of the hydrogen bonding between amide groups. In the isotropic phase (220°C and 240°C), however, the band for the stretching vibration of the amide N-H shifted to a lower frequency at 3420 cm<sup>-1</sup>. In this case, the smectic orientation of PAAD-H becomes disordered because the hydrogen bonding becomes less stable.

This paper demonstrates that the formation of the hydrogen bonding between

a) Number-average molecular weight determined with GPC, calibrated by standard polystyrenes.

secondary amide groups in liquid crystalline polymers acts effectively, forming the smectic phase with enhanced thermal stability.

#### **Acknowledgment**

Financial support of this Research by an unrestricted gift from Science University of Tokyo is gratefully acknowledged.

#### References

- J. C. Rowell, W. D. Phillips, L. R. Melby and M. Panar, J. Chem. Phys., 43, 3442 (1965).
   J. Barbara, M. Marcos and J. L. Serrano, Mol. Cryst. Liq. Cryst., 166, 61 (1989).
- 3. D. Demus and L. Richter, Texture of Liquid Crystals, Verlag Chemie, New York (1978).
- 4. X-ray scattering curves were measured with a Rigaku Rad 2B system with CuK<sub>α</sub>.
- 5. FT-IR spectra were measured with a Perkin Elmer 1600 series FT-IR.