Polymer Bulletin 39, 701–705 (1997)

Polymer Bulletin

Molecular packing of poly(azomethine)s having flexible (*n*-alkyloxy)methyl side chains in films

Heesub Kim, Wang-Cheol Zin

Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang 790-784, Korea

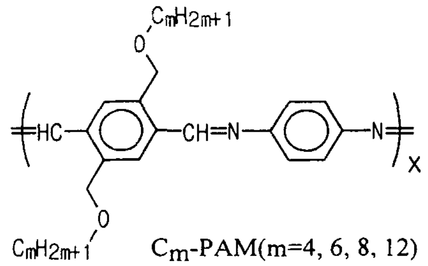
Received: 15 August 1997/Accepted: 21 October 1997

Summary

The molecular packing of poly(azomethine)s having (*n*-alkyloxy)methyl side chains in films was studied by wide-angle X-ray scattering. Solution-cast films on silicon wafer and melt-sheared films show the same type of molecular packing, i.e. the main chain layers are aligned parallel to the film surface but the main chains are macroscopically isotropic in the film surface plane. In the melt-sheared films, the shear does not orient the main chains but the main chain layers, which can be easily understood by their geometric shapes.

Introduction

In a number of recent publications(1-11) it has been shown that pendent flexible side chains attached to stiff main chains greatly enhances solubility and fusibility of the rigid-rod polymers and these polymers form a novel layered structure in their crystalline phase and mesophase. The layered structure is characterized by a segregated structure, in which the main chains form separate layers, with the flexible side chains occupying the space between the main chain layers. In addition, studies on solution-cast/melt-pressed films of rigid-rod poly(ester)s(12,13) and poly(phenylene)s(14) having flexible side chains indicate that main chain layers tend to be stacked parallel with respect to the film surface and main chains are macroscopically isotropic in the surface plane.



C_m-PAM(m=4, 6, 8, 12)

In our previous papers(15,16) we reported the preparation, crystal structure and phase behavior of poly(azomethine)s having (*n*-alkyloxy)methyl side chains (designated as C_m-PAMs(m=4, 6, 8, 12)). They were prepared by solution condensation of 2,4-bis((*n*-alkyloxy)methyl)terephthalaldehydes with *p*-phenylenediamine. It was found that in mesophase as well as in crystalline phase they form a layered structure in which main chain layers are separated by side chains.

In the present study, we report molecular packing of these polymers in solution-cast /melt-sheared films based upon X-ray studies. In the films, the main chain layers can have three ways of packing with respect to the substrate or film surface, as shown in Figure 1. Thus the objective of the present study is to investigate how the main chains layers are packed with respect to the substrate or film surface in the films.

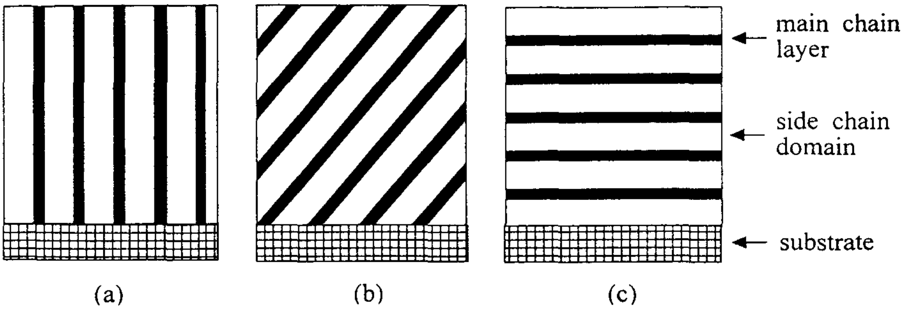


Figure 1. Schematic representation of molecular packing for the films. The main chain layers are packed perpendicular(a), tilted(b) and parallel(c) to the substrate surface.

Experimental

A melt-sheared film of C_{12}-PAM was prepared by shearing in the layered mesophase and subsequent quenching. Solution-cast films of C_{12}-PAM and C_8-PAM-B(15) were prepared by casting on a silicon wafer from a 0.5 wt% solution of C_{12}-PAM in *m*-cresol and C_8-PAM-B in hexamethylphosphoramide, respectively, using the following method. A small quantity of the polymer solution was spread on a silicone wafer. The solvent was slowly evaporated over a period of 7 days by applying vacuum at room temperature. This procedure resulted in a thin polymer film coated on the silicon wafer.

X-ray reflections ($2^\circ < 2\theta < 32^\circ$) were measured from a Rigaku-Denki X-ray generator using CuKα radiation and a graphite monochromator installed in front of the counter. The X-ray reflections for the solution-cast films on silicon wafer were measured in reflection mode while those for the melt-sheared films were measured in transmission mode.

Results and discussion

X-ray diffraction measurements confirmed the existence of layered structures in the solution-cast films on silicon wafer. Figure 2 shows X-ray diffractograms of the solution-cast films of C_{12}-PAM and C_8-PAM-B measured in reflection mode at room temperature, respectively. For comparison, X-ray diffractograms of powder samples are also included.

Detailed interpretation of the peaks of the powder patterns in Figure 2 leading to layered structures has already been described previously(16), and the schematic illustration for the layered structures is shown in Figure 3. The reflections A(20.8 and 16.2Å for C_{12}-PAM and C_8-PAM-B, respectively), with its higher orders, arise from the layer spacings between the main chain layers. The wide-angle reflections appearing in the

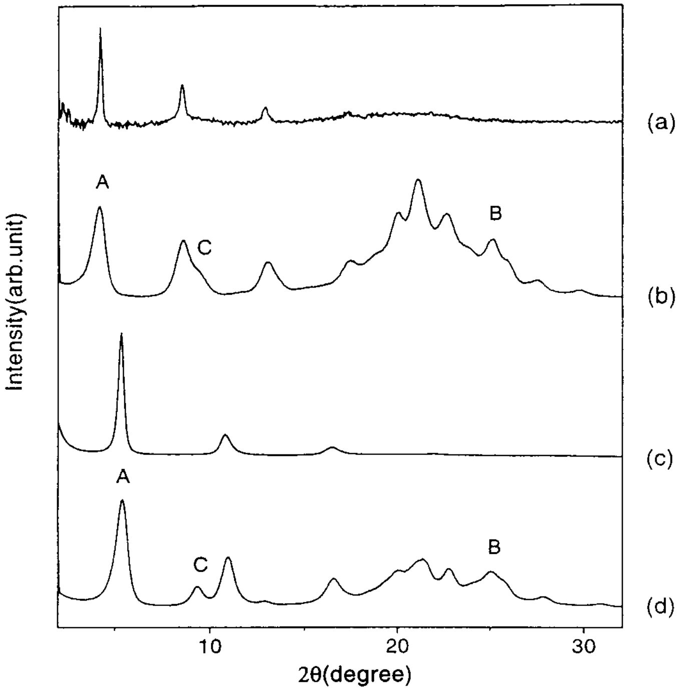


Figure 2. X-ray diffractograms of C_{12}-PAM and C_8-PAM-B measured in reflection mode at room temperature. (a) solution-cast film of C_{12}-PAM (b) powder sample of C_{12}-PAM (c) solution-cast film of C_8-PAM-B (d) powder sample of C_8-PAM-B

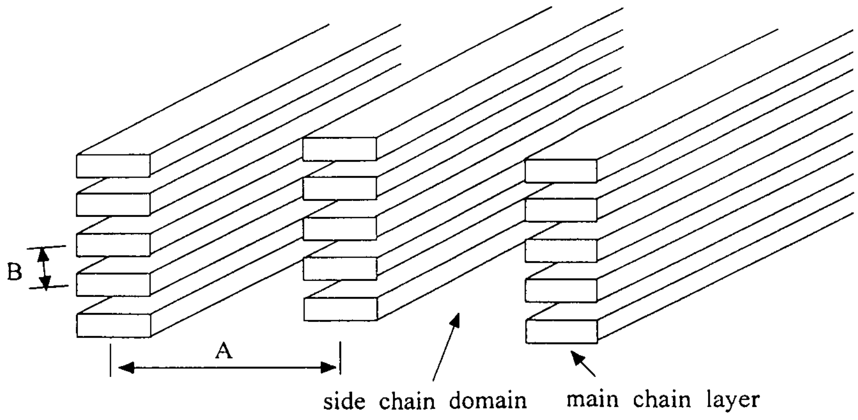


Figure 3. Schematic illustration of the layered structures of C_m-PAM.

$2\theta = 21\sim24^\circ$ region arise from the side chain crystals. The side chains, which are fully interdigitated and tilted with respect to the rigid main chain, come to occupy the space between the main chain layers. The reflections B and C arise from a lateral packing of main chains and a slipped structure of the repeat unit, respectively.

Compared to the X-ray pattern for the powder, the X-ray pattern for the film is greatly simplified. Only small-angle reflection with its higher orders, corresponding to the layer spacing, is observable. This demonstrates clearly that the main chain layers are spontaneously aligned parallel to the substrate surface, which is schematically illustrated in Figure 1(c). The main chains are believed to be macroscopically isotropic in the surface plane, which is based on the fact that there was no external force applied for the alignment of the main chains in a certain direction.

Melt-sheared films that were quenched from the layered mesophase showed the same type of molecular packing observed for the solution-cast films. Two X-ray diffractograms of the melt-sheared film of C_{12}-PAM are shown in Figure 4, in which patterns (a) and (b) are measured with the X-ray beam parallel and perpendicular to the film surface, respectively. It should be mentioned that each pattern is independent of the rotation of the films about the axis perpendicular to the film surface.

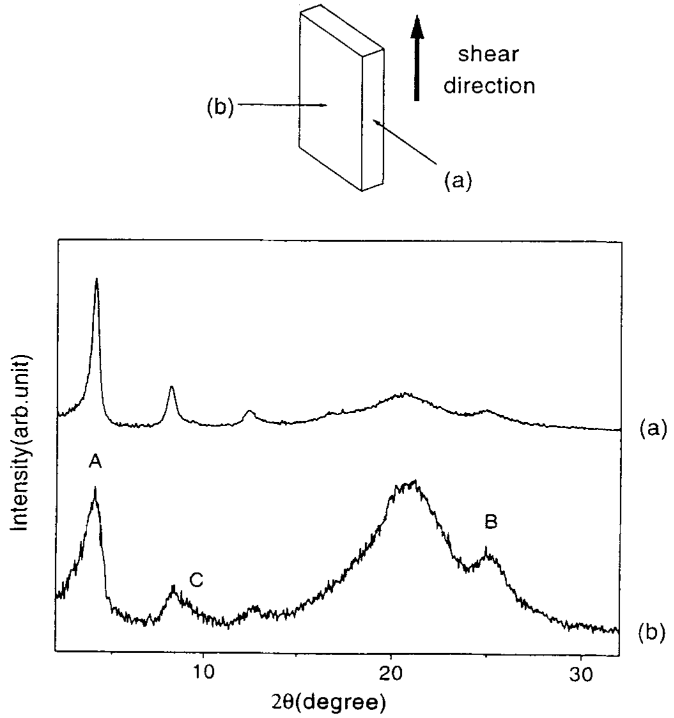


Figure 4. X-ray diffractograms of a melt-sheared film of C_{12}-PAM measured in transmission mode at room temperature. (a) X-ray beam exposed parallel to the film surface (b) X-ray beam exposed perpendicular to the film surface

Comparison of the two patterns shows that the reflections arising from the layer spacing are more prominent in pattern (a) than in pattern (b). These results strongly suggest that the main chain layers are aligned parallel to the film surface but the main chains are macroscopically isotropic in the surface plane. As a result, the shear does not orient the main chains but the main chain layers, which can be easily understood by their geometric shapes.

In conclusion, the solution-cast/melt-sheared films of C_m-PAMs exhibit the molecular packing that the main chain layers are packed parallel to the film surface. The parallel packing of the main chain layers to the surface has been also found in films of other rigid-rod polymers(12-14) having flexible side chains and thus seems to be a general phenomenon for films of rigid-rod polymers having flexible side chains.

Acknowledgements

This study was supported by Korean Ministry of Education through Research Fund.

References

1.Ballauff M (1986) Makromol. Chem. Rapid. Commun. 7:407
2.Wenzel M, Ballauff M, Wegner G (1987) Makromol. Chem. 188:2865
3.Rodriguez-Parada JM, Duran R, Wegner G (1989) Macromolecules 22:2507
4.Stern R, Ballauff M, Lieser G, Wegner, G (1991) Polymer 32: 11
5.Harkness BR, Watanabe J (1991) Macromolecules 24:6759
6.Steuer M, Horth M, Ballauff, M (1993) J. Polym. Sci. : Polym. Chem. Ed. 31:1609.
7.Watanabe J, Harkness BR, Sone M, Ichimura H (1994) Macromolecules 27:507
8.Kricheldorf HR, Domschke A (1994) Macromolecules 27:1509
9.Jung JC, Park S-B (1995) Polymer Bulletin 35:423
10.Kricheldorf HR, Domschke A (1996) Macromolecules 29:1337
11.Jung JC, Park S-B (1996) J. Polym. Sci.:Polym. Chem. Ed. 34:357
12.Schrauwen C, Pakula T, Wegner G (1992) Makromol. Chem. 193:11
13.Damman SB, Mercx FPM, Lemstra PJ (1993) Polymer 34:2726
14.McCarthy TF, Witteler H, Paulka T, Wegner G (1995) Macromolecules 28:8350
15.Park S-B, Kim H, Zin W-C, Jung JC (1993) Macromolecules 26:1627
16.Kim H, Park, S-B, Jung JC, Zin, W-C (1996) Polymer 37:2845