Evaluation of Molecular Orientation on Biopolyimide Film Using Polarized ATR/FT-IR

Saranyoo SORNKAMNERD[1], Hojoon SHIN[1], Shinji ANDO[2], and Tatsuo KANEKO[1*]

[1]*Energy and Environment Area, Japan Advanced Institute of Science and Technology (JAIST), Asahidai, Nomi, Ishikawa 923-1292, Japan*
[2]*Department of Chemical Science & Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan*

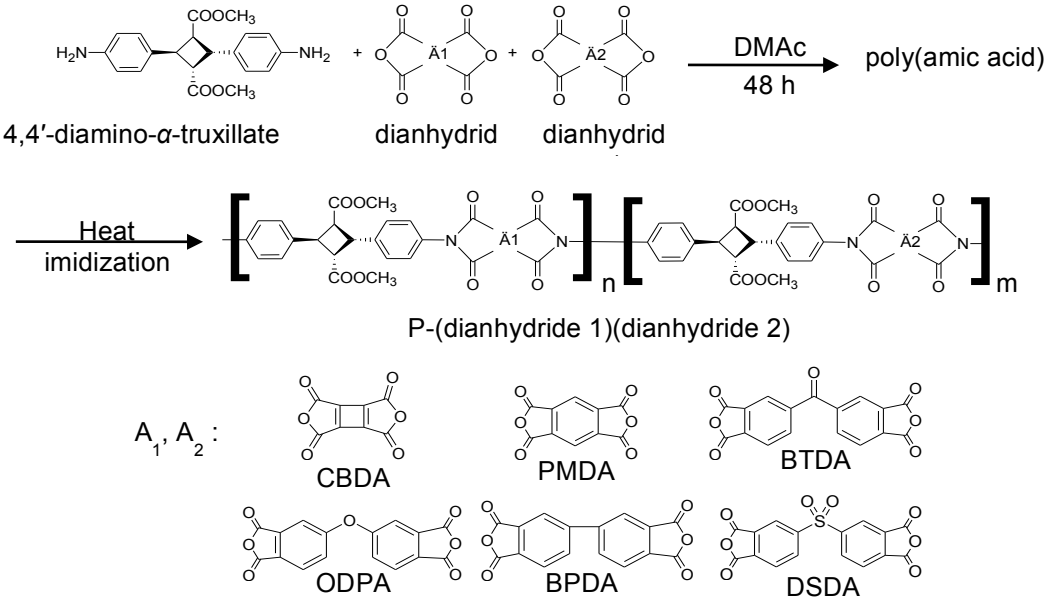
Abstract

We developed ductile biopolyimide (BPI) films derived from a renewable aromatic diamine, 4,4′ -diaminotruxillic acid, with a mixture of two different dianhydrides. The BPI copolymers show high thermal and mechanical performances which were effected by molecular chain orientation. Using ATR/FTIR technique we found CBDA, PMDA, BPDA homopolymer and their combination showed the highest in-plane orientation because of rigid structure.

1. Introduction

We have prepared bio-based polyimides (BPI) exhibiting high thermal and mechanical performances by polycondensation of photodimers of microbial 4-aminocinnamic acid with dianhydrides [1, 2]. The thermomechanical properties such as coefficient of linear thermal expansion are significantly affected by the orientation of BPI chains in solid films [3]. In this study, the orientation of the BPI chains was analyzed by ATR-FTIR spectroscopy [4], providing information on the three dimensional orientations of BPI chains by monitoring the IR absorption of C−N bond of which the dipolar moment is parallel to the BPI main chains. Moreover, the birefringence of the BPI films was quantitatively analyzed.

2. Results and Discussion



Scheme 1. Synthetic route and chemical structures of BPI polymers derived from 4,4′-diamino-*α*-truxillate with dianhydrides

The BPI films were prepared from aromatic diamine, 4,4'-diaminotruxillate dimethyl, with stoichiometric amounts of dianhydride monomers: CBDA, PMDA, BTDA, ODPA, BPDA, and DSDA **(Scheme 1)** [1]. Based on the ATR/FT-IR spectra of PI films (Nicolet AVATAR320 IR spectrometer), the orientation coefficients were estimated from the dichroic ratios of the absorption peak around 1363 cm-1 (υ(C-N) axial stretching) **(Table 1)**. The in-plane/out-of-plane birefringence was estimated from the refractive indices measured using a prism-coupler (Metricon, Model PC-2010) at a wavelength of 1310 nm. Both techniques revealed that the BPI films derived from the dianhydrides, CBDA, PMDA or BPDA exhibited higher degrees of in-plane chain orientation due to the rigid and planar conformations of the dianhydrides.

Table 1. Thermal, transparency, mechanical and orientation properties of polyimide films.

Polyimide	M_n [a] (×105)	M_w [a] (×105)	T_{10} [b] (°C)	T_g [c] (°C)	%T [d]	E [e] (GPa)	σ [e] (MPa)	ε [e] (%)	n_{av} [f]	Δn [g]	P_{200} [h]
P-CBDA	2.78	3.99	390		88	10.01±3.68	75±6.62	1.82±0.28	1.562	0.019	-0.269
P-PMDA	4.61	3.19	425		80	8.02±1.19	89±9.24	2.48±0.12	1.601	0.065	-0.277
P-BTDA	2.25	3.06	420	258	79	4.24±0.18	48±0.75	1.72±0.33	1.607	0.024	-0.139
P-ODPA	2.20	3.15	410	248	68	13.39±3.03	98±5.71	4.49±0.43	1.605	0.010	-0.074
P-BPDA	1.70	2.56	410	254	65	4.38±0.55	71±2.14	2.42±0.43	1.628	0.062	-0.208
P-DSDA	1.97	2.78	425	275	82	4.77±0.75	90±5.30	3.31±0.32	1.598	0.013	-0.113
P-CBDA/PMDA	7.31	10.8	415		89	4.2±0.46	79±21.8	2.8±0.65	1.582	0.041	-0.199
P-CBDA/BTDA	6.65	10.0	406	243	80	4.3±0.34	98±24.7	3.2±1.36	1.586	0.015	-0.148
P-CBDA/OPDA	4.88	6.78	408	243	86	3.5±0.23	63±1.8	2.1±0.14	1.587	0.010	-0.112
P-CBDA/BPDA	7.07	12.5	413	250	85	3.7±0.06	61±37.4	2.1±1.33	1.597	0.027	-0.186
P-CBDA/DSDA	7.86	9.88	399	245	85	3.1±0.15	67±9.3	2.5±0.38	1.581	0.006	-0.113
P-PMDA/BTDA	8.46	12.0	424		82	4.1±0.49	105±17.7	4.9±0.72	1.605	0.031	-0.181
P-PMDA/OPDA	6.93	10.6	418		83	2.9±1.01	65±24.1	3.5±0.60	1.609	0.034	-0.150
P-PMDA/BPDA	7.44	11.4	423		79	3.7±0.20	56±5.3	1.9±0.10	1.613	0.068	-0.217
P-PMDA/DSDA	7.78	44.4	412	270	74	3.8±0.46	82±14.5	2.9±0.38	1.598	0.024	-0.141
P-BTDA/OPDA	8.90	15.3	424	225	81	4.1±0.08	113±5.0	9.4±2.88	1.605	0.013	-0.118
P-BTDA/BPDA	8.13	12.2	425	225	86	4.4±0.38	110±11.9	3.0±0.81	1.613	0.023	-0.153
P-BTDA/DSDA	7.12	12.5	411	236	85	3.1±0.69	80±16.3	4.0±0.16	1.602	0.011	-0.089
P-OPDA/BPDA	8.30	13.1	425	208	82	3.9±0.67	28±6.9	0.9±0.14	1.622	0.025	-0.113
P-OPDA/DSDA	5.27	8.78	412	227	80	3.6±0.28	96±10.4	5.1±0.95	1.602	0.010	-0.079
P-BPDA/DSDA	6.54	9.94	414	243	83	3.9±0.39	66±1.1	2.2±0.31	1.605	0.017	-0.117
Kapton						2.8	63	12.8			

[a] The number-average molecular weight, M_n, weight-average molecular weight, M_w, and distribution of the polymer molecular weight. [b] 10% weight loss temperatures, T_{10}, were recorded by picking up the data from the TGA curve scanned at a heating rate of 10 °C/min under a nitrogen atmosphere. [c] The glass transition temperature, T_g, was measured by a DSC thermogram scanned at a heating rate of 10 °C/min under a nitrogen atmosphere.[d] The transmittance at 450 nm, *%T*, was measured by a UV/vis spectrophotometer. [e] The values of Young's modulus E, tensile strength σ, elongation at break ε, and strain energy were obtained from a tensiometer at room temperature. [f] The average of refractive index, n_{av}, *, was determined as* $n_{av}^2 = (2n_{\parallel}^2 + n_{\perp}^2)/3$. [g] The birefringences, Δn, *was determined as* $n_{\parallel} - n_{\perp}$ The in-plane, $n_{\parallel}$, out-of-plane, $n_{\perp}$, refractive index were measured using the Metricon, Model PC-2000 machine at λ= 1310 nm. [h] The orientation coefficients, P_{200}, *was* calculated from the C-N bonds using ATR/FTIR technique.

3. Conclusion

In this study, the effect of dianhydried on biopolyimide (BPI) chain orientation was investigated. Because of the chemical structure CBDA, PMDA and BPDA are rigid molecule thus BPI composed of them not free rotate and highly in-plane orientation.

Acknowledgement: The researches were financially supported by MOE project.

References:

[1] Suvannasara, P., et al. *Macromolecules*, 47(5), 1586-1593 (2014).
[2] Shin, H., Kaneko, T. et al. *Ind. Eng. Chem. Res.* 55(32), 8761-8766 (2016).
[3] Park, S.C., Liang, Y., and Lee, H.S. *Macromolecules*, 37(15), 5607-5614 (2004).
[4] Flournoy, P.A. Schaffers, W.J. *Spectrochimica Acta*, 22(1), 5-13 (1966)