Polymer Bulletin 60, 49–55 (2008)
DOI 10.1007/s00289-007-0839-9

Polymer Bulletin

Radical polymerization of fumaramide and fumaramate derivatives for homogeneous Langmuir monolayers

Tsuyoshi Michinobu[a,b], Kazuya Nakada[b], Kiyotaka Shigehara[a,b] (✉)

[a] Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
[b] Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan
E-mail: jun@cc.tuat.ac.jp

Received: 9 July 2007 / Revised version: 3 September 2007 / Accepted: 9 September 2007

Summary

The radical polymerization of a series of fumaramides and fumaramates, prepared from the reaction of various amines with fumaroyl dichloride and fumaric chloride isopropyl ester, respectively, was investigated. Although the polymerization reactivity of the *N*,*N*,*N*',*N*'-tetrasubstituted fumaramides and *N*,*N*-disubstituted fumaramates was low, *N*-isopropyl fumaramate readily furnished the corresponding high molecular weight polymer. The highest number average molecular weight (M_n) of 15,400 was obtained from the emulsifier-free emulsion polymerization in the presence of VA-086 as the initiator. The decomposition temperature of the obtained polymer was determined to be 299°C. The π-A isotherm of the polymer indicated the formation of stable Langmuir monolayers with a limiting molecular area (per macromolecular repeating unit) of ca. 26 Å^2.

Introduction

The preparation of homogeneous ultrathin films with precise control of the film thickness down to a monolayer scale is fundamentally important for current electronic applications [1,2]. Although small molecular weight amphiphilic molecules readily form stable and homogeneous Langmuir monolayers, they have major drawbacks, such as a low thermostability and limited mechanical properties. Polymers are a good solution for these problems, but there is another requirement for the preparation of the Langmuir and Langmuir-Blodgett films of polymers, that is, their extended conformations at the air-water interface.

We have previously reported the formation and the electronic properties of stable Langmuir-Blodgett films of the poly(dialkyl fumarate)s [3-5]. Poly(dialkyl fumarate)s, typically prepared by the radical polymerization of dialkyl fumarates with bulky alkyl ester groups, are classified as a poly(substituted methylene) type polymer and thereby possess a rigid main-chain moiety, as represented by the α value of 1 in the Mark-Houwink-Sakurada equation [6-8]. This rigid main-chain leads to a relatively high glass transition temperature (T_g) of >250°C, which is also reflected by the temperature independence of the π-A isotherms of the poly(dialkyl fumarate)s [3,9].

To further pursue the thermal stability of the poly(substituted methylene) type ultrathin films, we decided to introduce amide substituents as a side chain to utilize the intramolecular hydrogen bonding interactions. The successful synthesis of poly(*N*,*N*,*N*',*N*'-tetraalkyl fumaramide)s and poly(*N*,*N*-dialkyl fumaramate)s by either the radical polymerization of the fumaramide and fumaramate monomers, respectively, or the polymer reactions of poly(fumaric acid) have in the past been reported [10-12]. We now report for the first time the higher radical polymerization reactivity of the *N*-alkyl fumaramate monomer with respect to the previously reported fumaramide and fumaramate monomers, improved thermal stability of the resulting polymer, and formation of stable Langmuir films with a limiting molecular area (per macromolecular repeating unit) of ca. 26 Å^2.

Experimental

Materials

Chemicals were purchased from Kanto, Tokyo Kasei, and Wako, and used as received. Reagent grade solvents and water were purified by distillation twice and immediately used. Compounds **1** [10], **2** [10], **3** [13], and **4** [11] were prepared according to literature procedures.

Instruments

A computer-controlled home-made LB apparatus similar to that reported in the literature [14] was employed for preparation of Langmuir films. The π-A isotherm measurement was carried out at 21 ± 1°C. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL model AL200 spectrometer at 20°C. Chemical shifts are reported in ppm downfield from $SiMe_4$, using the solvent's residual signal as an internal reference. Coupling constants (J) are given in Hz. The resonance multiplicity is described as s (singlet), d (doublet), sep (septet), and m (multiplet). Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 spectrometer. Gel permeation chromatography (GPC) was measured on a JASCO system (PU-980, CO-965, RI-930, UV-970, and AS-950) equipped with polystyrene gel columns using chloroform as an eluent at a flow rate of 1.0 ml min^{-1} after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was carried out on a Rigaku Thermoplus TG 8120 (10°C min^{-1}).

Synthesis

*Isopropyl N,N-diisopropyl fumaramate (**5**)*

To a THF solution of diisopropylamine (15.2 g, 0.150 mol) and triethylamine (15.3 g, 0.150 mol) at 0°C, a THF solution of fumaric chloride isopropyl ester (17.7 g, 0.100 mol) was dropwise added. After stirring for 24 h, the mixture was filtered, and the filtrate was evaporated to ca. 20 ml, which was poured into a 3N HCl aqueous solution. Chloroform was added to this mixture and the organic layer was collected, which was washed with water and dried over sodium sulfate. After filtration, removal of the solvents in vacuo followed by vacuum distillation afforded **5**. Yield 20%. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.23–1.45$ (m, 18 H), 3.62–3.80 (m, 1 H), 3.96–4.14 (m, 1 H), 5.10 (sep, J = 6 Hz, 1 H), 6.57 (d, J = 15 Hz, 1 H), 7.38 ppm (d, J = 15 Hz, 1 H);

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.1, 21.4, 45.7, 68.0, 129.0, 136.7, 164.0, 165.0 ppm; IR (liquid film): ν = 2984, 2933, 1713, 1621, 1448, 1374, 1338, 1300, 1270, 1184, 1106, 1046, 986 cm^{-1}.

*Isopropyl N-methyl-N-phenyl fumaramate (**6**)*

Following the synthetic procedure of **5**, **6** was prepared from *N*-methylaniline (24.1 g, 0.225 mol) and the fumaric chloride isopropyl ester (26.5 g, 0.150 mol). To the crude product in chloroform, activated carbon was added with vigorous stirring. Removal of the activated carbon followed by recrystallization from *n*-hexane or *n*-heptane afforded **6**. Yield 54%. M.p. 66°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.22 (d, J = 6 Hz, 6 H), 3.38 (s, 3 H), 5.00 (sep, J = 6 Hz, 1 H), 6.84 (s, 1 H), 7.17 (d, J = 8 Hz, 2 H), 7.36–7.48 ppm (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.8, 37.8, 68.5, 127.0, 128.0, 129.9, 131.5, 134.0, 142.8, 164.1, 165.1 ppm; IR (KBr): ν= 3040, 2977, 2928, 1721, 1666, 1634, 1594, 1493, 1462, 1414, 1384, 1296, 1283, 1252, 1176, 1113, 984, 902, 831, 772, 760, 702, 647, 569 cm^{-1}.

*Isopropyl N-isopropyl fumaramate (**7**)*

Following the synthetic and purification procedure of **6**, **7** was prepared from isopropylamine (8.90 g, 0.150 mol) and fumaric chloride isopropyl ester (17.7 g, 0.100 mol). Yield 41%. M.p. 69°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ= 1.21 (d, J = 6 Hz, 6 H), 1.29 (d, J = 6 Hz, 6 H), 4.20 (sep, J = 6 Hz, 1 H), 5.08 (sep, J = 6 Hz, 1 H), 6.13 (br s, 1 H), 6.78 (d, J = 15 Hz, 1 H), 6.92 ppm (d, J = 15 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.8, 22.8, 42.0, 68.8, 120.8, 126.5, 152.8, 155.2 ppm; IR (KBr): ν= 3247, 3070, 2984, 1716, 1660, 1632, 1554, 1468, 1359, 1297, 1182, 1113, 999 cm^{-1}.

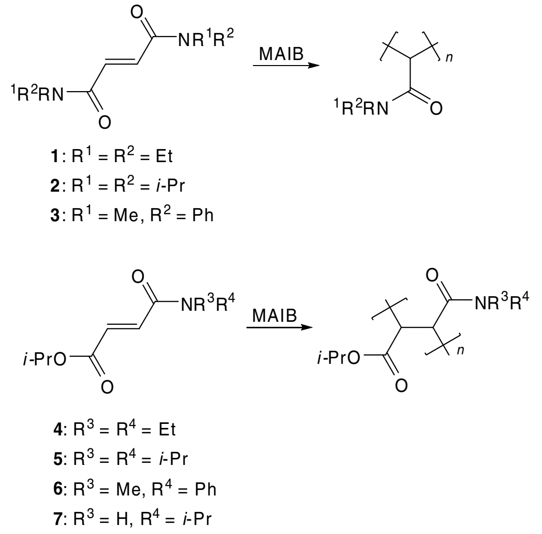
Polymerization

The bulk or solution polymerization was carried out under reduced pressure in a sealed glass tube in the presence of dimethyl 2,2-azobisisobutyrate (MAIB) as the initiator. After storing in a thermostated bath at the given temperature, the mixture was cooled to room temperature. The glass tube was opened and the polymerization solution was poured into a large amount of cold *n*-hexane, yielding a white precipitate. The precipitated polymers were collected by either centrifugation or filtration and dried in vacuo. The emulsifier-free emulsion polymerization of **7** (3.0 g) in water (50 ml) was carried out in the presence of 1.0 mo% VA-086 (Tokyo Kasei) as the water-soluble azo-type initiator. After stirring at the agitation rate of 3000 rpm at 80°C for 7 days, the reaction mixture was rapidly cooled to room temperature. The resulting precipitate was extracted with toluene, washed with hot *n*-hexane, and reprecipitated into cold *n*-hexane, yielding the corresponding polymer.

Results and discussion

The fumaramide and fumaramate monomers were prepared from the reaction of various amines with fumaroyl dichloride and the fumaric chloride isopropyl ester, respectively, and unambiguously characterized by ^{1}H and ^{13}C NMR and FT-IR spectroscopies.

The conventional radical polymerization of the monomers was carried out either in a toluene solution or in bulk with heating in the presence of MAIB as the initiator (Scheme 1 and Table 1). It was reported that dialkyl fumarates with bulky ester substituents, such as the isopropyl group, readily furnish the corresponding polymers by radical polymerization and that the introduction of further bulkier alkyl substituents results in a decrease in the polymerization reactivity [15,16]. This tendency is supposed to be more significant for the fumaramide and fumaramate monomers due to the increased number of side-chain substituents. For example, it was reported that the polymerization of *N*,*N*,*N*',*N*'-tetraethyl fumaramide **1** in the presence of 1,1'-azobiscyclohexane-1-carbonitrile (ACN) as an initiator efficiently proceeded to yield a high molecular weight polymer, whereas the *N*,*N*,*N*',*N*'-tetraisopropyl fumaramide **2** did not provide the corresponding polymer by solution polymerization with ACN [10]. Note that the introduction of bulkier substituents leads to an increase in the melting points of the monomers (e.g., M.p. of **2**: 146°C), and accordingly, prevents the bulk polymerization. We examined the polymerization of these monomers with a different initiator, MAIB, and found that **2** can be polymerized in toluene at 60°C for 50 days, albeit in a very low yield, giving the corresponding polymer with an M_n of 2400 and polydispersity (M_w/M_n) of 1.54. However, **3** possessing the bulkier phenyl substituents (M.p.: 194°C) was not polymerized at all under similar conditions. The general behavior that the bulk polymerization is more efficient than the solution polymerization was observed for **1**.



1: $R^1 = R^2 = Et$
2: $R^1 = R^2 = i\text{-}Pr$
3: $R^1 = Me, R^2 = Ph$

4: $R^3 = R^4 = Et$
5: $R^3 = R^4 = i\text{-}Pr$
6: $R^3 = Me, R^4 = Ph$
7: $R^3 = H, R^4 = i\text{-}Pr$

Scheme 1

There was a similar trend in the polymerization of the isopropyl *N*,*N*-dialkyl fumaramates **4**-**6**. The bulk polymerization of diethyl fumaramate **4** afforded a small amount of oligomers, whereas the polymerization of **5** and **6** with bulkier substituents did not proceed at all. These results are in contrast to the *N*,*N*'-disubstituted fumaramides, which do not homopolymerize under any conditions so far attempted [10,17]. The least sterically hindered monomer, isopropyl *N*-isopropyl fumaramate **7**, reasonably showed the greatest polymerization reactivity. The bulk polymerization at 80°C for only 2 days afforded the corresponding high molecular weight polymer with an M_n of 8700 and M_w/M_n of 2.07 in 34% yield. Similar to other fumaramides and fumaramates, the polymerization reactivity slightly decreased upon the addition of solvents (in this case, toluene). Surprisingly, when the emulsifier-free emulsion polymerization was applied, further improvement in the polymerization reactivity was achieved. The appropriate water solubility of **7** and a low propagating radical concentration in the emulsions are supposed to efficiently prevent the coupling of the radicals or the termination process of the polymerization. In this study, we utilized the distinct solubility difference between **7** and the corresponding polymer in hot hexane for purification, thus yielding the highest M_n of 15,400 with the narrow M_w/M_n of 1.70. The NMR spectra of the polymers indicated the disappearance of the vinylene protons at 6.8–6.9 ppm. In the IR spectra, the peaks ascribed to the deformation vibration of the *trans* vinylene (e.g., 999 cm^{-1} for **7**) also disappeared upon polymerization.

Table 1 Radical polymerization of the fumaramides **1**-**3** and the fumaramates **4**-**7**

Monomer	Solvent	Temp / °C	Time / days	Yield / %	M_n	M_w/M_n
1[a]	Bulk	90	10	trace[g]	5200	1.64
1[a,b]	Toluene	60	50	—	—	—
2[a,b]	Toluene	60	50	trace[g]	2400	1.54
3[a,c]	Toluene	80	47	—	—	—
4[a]	Bulk	100	31	trace[g]	900	2.36
5[d]	Bulk	80	15	—	—	—
6[a]	Bulk	80	37	—	—	—
7[a]	Bulk	80	2	34	8700	2.07
7[a,e]	Toluene	80	2	30	6000	2.25
7[f]	—	80	7	49	15400	1.70

[a] The polymerization was carried out with 1.0 mol% of MAIB as the initiator. [b] Monomer concentration of 1.0 M. [c] Monomer concentration of 0.5 M. [d] 2.0 mol% of MAIB was used. [e] Monomer concentration of 6.0 M. [f] Emulsifier-free emulsion polymerization in the presence of 1.0 mol% of VA-86. [g] Less than 1.0% yield.

The thermal stability of the polymer of **7** was investigated by thermogravimetric analysis (TGA) (Figure 1). The noticeable decomposition started at ca. 265°C and the decomposition temperature determined by derivative thermogravimetry was 299°C. The decomposition profile is similar to those of the previously reported polymethylene-type polymers and the decomposition temperature is comparable to that of the poly(*N*,*N*-dialkyl fumaramate)s [11]. Since the decomposition

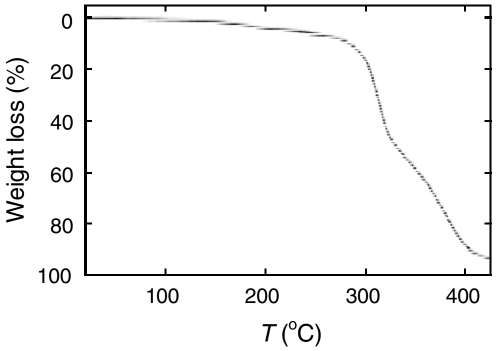


Figure 1. Thermogravimetric analysis of the polymer of **7** at the heating rate of 10°C min^{-1}.

temperatures of the poly(fumaramide)s and poly(fumaramate)s are higher than those of the poly(fumarate)s, intramolecular hydrogen bonding must play an important role in improving the thermal stability.

The π-A isotherm of **7** indicated the formation of a stable Langmuir monolayer with a limiting molecular area (per macromolecular repeating unit) of ca. 26 Å^2 and a collapse pressure of ~35 mN m^{-1} (Figure 2). As compared to the limiting fumarate unit areas of 32, 34, and 38 Å^2 for the poly(diisopropyl fumarate), poly(di-*tert*-butyl fumarate), and poly(dicyclohexyl fumarate), respectively, the limiting fumaramate unit area is much smaller [3]. This result highlights the well-packed, homogeneous ultrathin film formation of the poly(fumaramate)s presumably caused by the intramolecular hydrogen bonding interactions. Together with the steep inclining behavior and the relatively high collapse pressure of the π-A isotherm, the poly(fumaramate)s will be a versatile component for fabrication of stable Langmuir-Blodgett films.

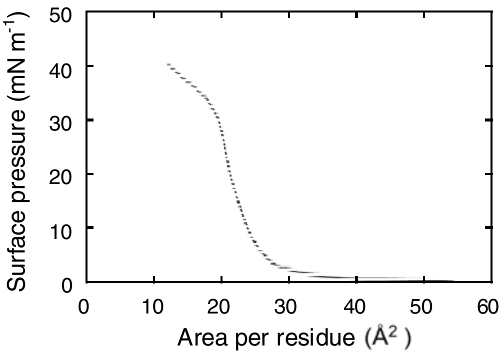


Figure 2. π-A Isotherm of the polymer of **7** at 23 ± 1°C on pure water.

Conclusions

We have investigated the radical polymerization of a series of fumaramide and fumaramate derivatives and found that the steric effect of the substituents on the polymerization capability is more significant than the dialkyl fumarates. Thus, *N*-isopropyl fumaramate **7** furnished the highest molecular weight polymer among the examined monomers. The obtained polymer possesses both an improved thermal stability and ultrathin film formation capability at the air-water interface as compared to the poly(dialkyl fumarate)s, probably due to intramolecular hydrogen bonding interactions. Further investigations on the Langmuir-Blodgett film preparation and the electronic applications are worthwhile for future work.

Acknowledgements. This work was supported in parts by a Grant-in-Aids from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. Kajiyama T, Kojio K, Tanaka K (2004) Adv Colloid Interface Sci 111: 159
2. Watanabe H, Vendamme R, Kunitake T (2007) Bull Chem Soc Jpn 80: 433
3. Shigehara K, Hara M, Nakahama H, Miyata S, Murata Y (1987) J Am Chem Soc 109: 1237

4. Shigehara K, Murata Y, Amaya N, Yamada A (1989) Thin Solid Films 179: 287
5. Chizaki M, Abe H, Iwa H, Tomokiyo R, Shigehara K, Amaya N, Kaiya N, Iimura Y, Kobyashi S (1995) Jpn J Appl Phys 34: 2411
6. Otsu T, Ito O, Toyoda N, Mori S (1982) Makromol Chem Rapid Commun 2: 725
7. Otsu T, Yasuhara T, Shiraishi K, Mori S (1984) Polym Bull 12: 449
8. Otsu T, Yoshioka M (1992) Macromolecules 25: 1615
9. Hayashi T, Ito S, Inogi, Y, Yamamoto M, Matsumoto A (1997) Eur Polym J 33: 770
10. Matsumoto A, Fukushima K, Otsu T (1991) J Polym Sci Part A: Polym Chem 29: 1697
11. Matsumoto A, Kotaki R, Otsu T (1991) J Polym Sci Part A: Polym Chem 29: 1707
12. Oyama T, Fukui T, Naka K, Chujo Y (1999) Polym Bull 43: 183
13. Hino T, Shioiri, T (1960) Chem Pharm Bull 8: 839
14. Furuno T, Sasabe H, Nagata R, Akaike T (1985) Thin Solid Films 133: 141
15. Otsu T, Shiraishi K, Matsumoto A, Amaya N, Mori S (1985) Polym Commun 26: 367
16. Azuma C, Ogata N (1972) Kobunshi Kagaku 29: 254
17. Otsu T, Yasuhara T, Matsumoto A (1988) J Macromol Sci Chem A25: 537