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Effect of Component Mobility on the Properties of Macromolecular [2]Rotaxanes

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Abstract: *Macromolecular [2]rotaxanes comprising a polymer axle and crown ether wheel were synthesized to evaluate the effect of component mobility on the properties of the axle polymer, especially its crystallinity. Living ring-opening polymerization of δ-valerolactone with a pseudorotaxane initiator with a hydroxy group at the axle terminus was followed by end-capping with a bulky isocyanate. This yielded macromolecular [2]rotaxanes (M2Rs) possessing polyester axles of varying molecular weights. The crystallinity of the axle polymers of two series of M2Rs, with either fixed and movable components, was evaluated by differential scanning calorimetry. The results revealed that the effect of component mobility was significant in the fixed and movable M2Rs with a certain axle length, thus suggesting that the properties of the axle polymer depend on the mobility of the polyrotaxane components.*

Polyrotaxanes are attracting considerable attention owing to their wide application range derived from the structural characteristics of their topological bonding and the dynamic nature of their components.[1] The synthesis and applications of primarily main-chain-type polyrotaxanes[2] have been extensively studied for two decades. However, there are few reports that describe the relationship between the chemical structure and properties of polyrotaxanes. Particularly, the effect of the presence of a wheel component on the properties of the axle polymer is an ongoing investigation. The research groups of Beckham and Gibson independently reported that melting (T_m) and glass transition (T_g) temperatures of the axle polymers of main-chain-type polyrotaxanes are lowered in the presence of wheel components.[3] We also reported that the T_g values of polyrotaxane axle polymers decrease with increasing numbers of wheel components. Moreover, the interaction between the axle and wheel components also affects the T_g of polyrotaxane.[4] These results demonstrate that the wheel component of polyrotaxanes clearly affects the properties of the axle polymer, especially the phase-transition temperature. However, detailed elucidation of the effect of the rotaxane structure remains difficult. This is because the polyrotaxanes studied thus far contain many wheel components on a single axle polymer. Moreover, the interaction between components and component mobility is complicated in these systems. Therefore, structure-definite polyrotaxanes should be used to clarify how the wheel component affects the properties of the axle polymer chain. Structure-definite polyrotaxanes are also known as macromolecular [2]rotaxanes (M2Rs), the simplest polyrotaxanes, which comprise a polymer chain and a ring. M2Rs have great potential for use in molecular machines[5] and block-copolymer technologies[6] owing to their controllable location, mobility, and deslippage of components. Fustin et al. recently prepared a metal-templated M2R,[7] whereas we established a synthetic method toward M2Rs comprising polyester axles and one crown ether wheel.[8] With M2Rs, we began to evaluate the effect of component mobility on the properties of the axle polymer. As shown in Figure 1, M2R-F has fixed components linked by strong attractive interactions, the *sec*-ammonium/crown ether interaction between the axle and wheel components, which is indispensable for the synthesis of M2Rs. Meanwhile, the components become movable on removal of these interactions through chemical treatment to yield M2R-M, thus making it possible to clarify the effect of component mobility.

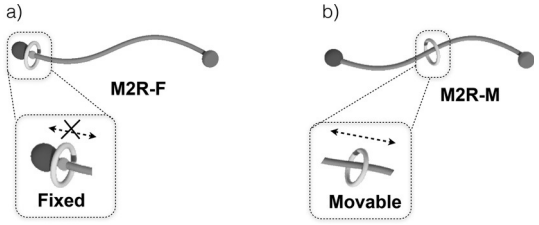

Figure 1. Macromolecular [2]rotaxanes (M2Rs) with fixed (a) and movable (b) components to investigate the effect of component mobility.

Herein, we describe the synthesis of a series of M2Rs with components that are either fixed or movable. Moreover, their component-mobility-dependent properties, with emphasis on the crystallinity of the axle polymer, were studied by differential scanning calorimetry (DSC). The present work will provide important information on polyrotaxanes because the effect of the wheel component on the properties of the axle polymer was studied for the first time, which was achieved by using structure-definite polyrotaxanes (M2Rs) consisting of one wheel component to one polymer axle.

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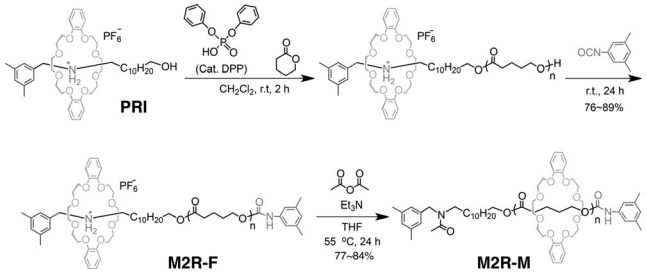
To evaluate the effect of the wheel component on the properties of the axle polymer component, we chose to investigate the crystallinity of the polymer, which is a suitable probe since it is affected by component mobility, by using M2Rs bearing crystalline polyester axles. Poly(δ-valerolactone) (PVL) and 24-crown-8 ether (DB24C8) were selected as the axle and wheel components, respectively. M2Rs with varying polymerization degrees were synthesized through living ring-opening polymerization of δ-valerolactone with pseudorotaxane initiator (PRI) by controlling their feed ratio. Subsequent end-capping of the propagating OH end was then performed with 3,5-dimethylphenyl isocyanate, as shown in Scheme 1 [($[M]_0/[I]_0$) = 10, 15, 20, 35, 50, and 100], according to our previously reported method.[8] Macromolecular



Scheme 1. Synthesis of macromolecular [2]rotaxanes with fixed (M2R-Fs) and movable components (M2R-Ms).

[2]rotaxanes with fixed components (M2R-Fs) were synthesized with a crown ether on the *sec*-ammonium moiety because the interaction with DB24C8 is sufficiently strong to prevent translation of the components, which also form stable PRI.. The movable M2R-Ms were prepared through N-acetylation of the *sec*-ammonium moiety of M2R-Fs with acetic anhydride in the presence of triethylamine (Scheme 1). The difference in mobility between M2R-F and M2R-M was discussed in our previous report.[8]

Table 1 summarizes the M2R synthesis results. Their molecular weights corresponded to the feed ratio, and the polydispersity index was relatively narrow in each case, which indicates that living polymerization proceeded successfully. The chemical structures were determined by ^{1}H NMR spectroscopy (Figure S2) and MALDI-TOF-MS (Figure S3-7), which demonstrated successful synthesis of both M2R-Fs and M2R-Ms.

Crystallization behavior was investigated by DSC. Figure 2 shows the melting traces of M2R-Fs and M2R-Ms in terms of polymerization degree, that is, axle polymer length. The M2R-F series (Figure 2a) showed a single endothermic peak over the range of 38–60 °C for M2R-Fs with a degree of polymerization (DP) higher than 15 (M2R20-F–M2R100-F). These melting peaks are attributed to a phase transition of the PVL axle from crystalline to amorphous. This suggests that M2R-Fs with shorter axle polymers cannot form the folded lamellar crystal (Figure 3a).[9] Meanwhile, such an endothermic peak was observed for M2R-Ms with higher than 20 DP (M2R35-F-M2R100-F; Figure 2b). This indicates the presence of a critical point. Namely, that the crystallinities

Table 1: Polymerization results for macromolecular [2]rotaxanes (M2Rs) with different DPs[a] and their melting properties.

M2R	$[M]_0/[I]_0$	Yield[b] [%]	DP[c]	M_n[d] [kDa]	M_w/M_n[d]	T_m[e] [°C]	ΔH_m[f] [J g^{-1}]
M2R10-F	10	86	10	1.4	1.3	–[g]	–[g]
M2R10-M	–	77	10	1.6	1.3	–[g]	–[g]
M2R15-F	15	76	14	1.6	1.4	–[g]	–[g]
M2R15-M	–	80	14	1.8	1.4	–[g]	–[g]
M2R20-F	20	87	17	2.3	1.3	42	39
M2R20-M	–	79	17	2.4	1.3	–[g]	–[g]
M2R35-F	35	79	33	2.7	1.3	39	59
M2R35-M	–	78	33	2.8	1.3	32	57
M2R50-F	50	87	49	3.6	1.3	42	61
M2R50-M	–	77	49	3.8	1.3	40	60
M2R100-F	100	89	97	4.9	1.2	44	68
M2R100-M	–	84	97	5.0	1.3	42	69

[a] Polymerization conditions: $[I]_0$ = 40 mmol L^{-1}, $[DPP]_0/[I]_0$ = 1, and ambient temperature. [b] Isolated yield by preparative GPC eluted with $CHCl_3$. [c] Degree of polymerization determined by ^{1}H NMR. [d] Determined by GPC eluted with THF on the basis of polystyrene standards. [e] Melting temperature. [f] Melting enthalpy. [g] Not observed. The DSC data were given on the basis of the second heating at a heating rate of 10 °C min^{-1}. [M] = δ-valerolactone, [I] = PRI, [DPP] = Diphenyl phosphate.

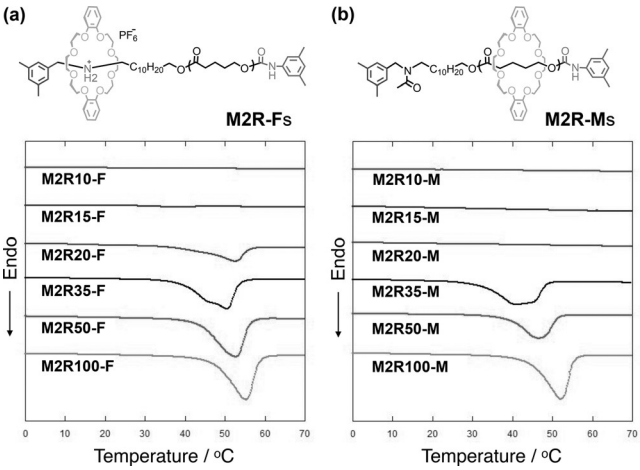


Figure 2. DSC curves during heating of M2R-Fs (a) and M2R-Ms (b) with different DPs (second heating) at a heating rate of 10 °C min^{-1}.

of M2R20-F and M2R20-M differ, with M2R20-M being an amorphous polymer and M2R20-F being a crystalline polymer. The difference based on the component mobility can be explained by assuming that the liberated crown ether wheel disturbs the crystallization of the polyester axle chain through its translation on the axle polymer in M2R20-M (Figure 3b). This assumption was supported by a control experiment using PVL with 17 DP in the absence of the wheel component (PVL20, prepared independently), which has a structure nearly identical to that of the M2R20-F axle component. The DSC profile (Figure S11 in the Supporting Information) showed melting behavior similar to that of M2R20-F. Therefore, it may be concluded that the fixed crown ether wheel does not affect axle polymer crystallization, whereas the movable wheel hinders it.

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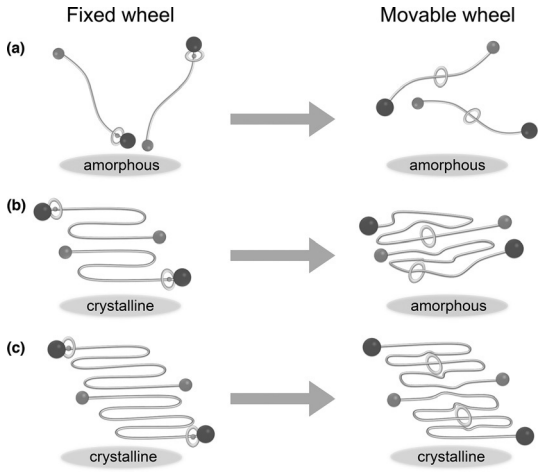

Figure 3. Schematic illustration of the crystallization behavior of the axle polymer of M2Rs in terms of component mobility and degree of polymerization: a) DP = 10, 14, b) DP = 17, and c) DP = 33, 49, and 97.

The melting temperature (T_m) and enthalpy (ΔH_m) values obtained by DSC are summarized in Table 1. M2R35-M shows a lower T_m value than M2R35-F, thus suggesting that the presence of the movable wheel lowers the T_m, although both are crystalline (Figure 3c). In the case of M2Rs with over 50 DP (M2R50, M2R100), no significant difference in T_m and ΔH_m were observed, thus suggesting that the component mobility has a negligible effect on the axle polymer properties when the axle polymer has sufficient length. Since the crystallization temperature (T_c) and enthalpy (ΔH_c) of the M2Rs in the cooling scan (Figure S8 and Table S1) were consistent with their melting behaviors, the presence of the critical point at approximately 17 DP should be emphasized.

To clarify the effect of component mobility on the polymer properties, we examined the isothermal crystallization behavior of M2R50s and M2R100s. The normalized crystallinity of M2Rs and PVLs was measured at a specific crystalline temperature (T_{sc}; 34 °C for M2R-50s and 38 °C for M2R-100s) for comparison, that is, the ratio of ΔH_m to ΔH^* defined as the melting enthalpy obtained by nonisothermal measurement with a heating rate of 10 °C min^{-1}. The results plotted against the isothermal crystallization time are shown in Figure 4.

M2R50-F and M2R100-F demonstrated near-identical crystallization behavior to the corresponding independently prepared PVLs (Figure 4a), thus suggesting that the ionic structure has a negligible effect on the crystallization behavior, although they crystallized faster than the corresponding PVLs. Conversely, M2R50-M and M2R100-M demonstrated slow crystallization compared to M2R50-F and M2R100-F. Meanwhile, M2R50-M crystalized much slower than M2R100-M, which is consistent with the assumption that the effect of component mobility becomes significant when the translational length of the axle chain is short, as mentioned above.

To verify the effect of component mobility on the crystal structure, WAXD measurements were employed for M2R35-F and M2R35-M (Figure S13). The WAXD profiles were

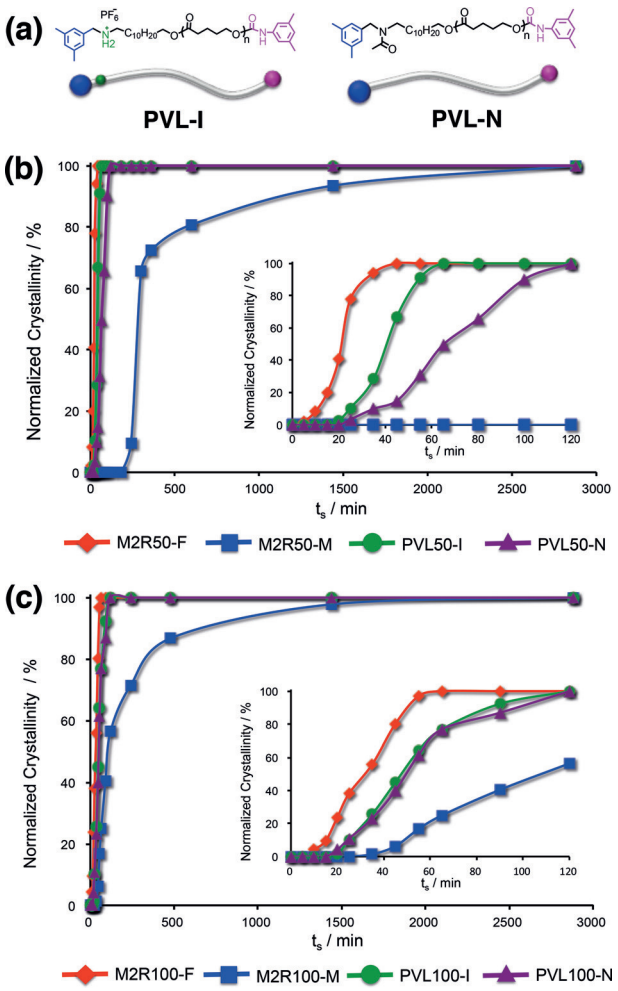

Figure 4. Time-dependent crystallinity of M2Rs. a) Structures of PVL-I and PVL-N. b,c) Crystallinity measured by DSC at a constant temperature (T_{sc}): 34 °C for M2R-50s and PVL50s (b) and 38 °C for M2R-100s and PVL100s (c). 100% crystallinity = melting enthalpy obtained by nonisothermal measurement with a heating rate of 10 °C min^{-1}.

identical, whereas the crystallinities of M2R35-F and M2R35-M were 27% and 30%, respectively. These results indicate that M2R35-F and M2R35-M form the same crystal structure and crystallinity; however, the crystallization behavior was seemingly affected by the movable wheel.[9]

In summary, we have synthesized macromolecular [2]rotaxanes (M2Rs) of varying molecular weights comprising PVL axles and one crown ether wheel to clarify the effect of component mobility on the properties. Two series of M2Rs, M2R-F and M2R-M, were synthesized to have fixed and movable components, respectively. Through detailed studies using DSC, we identified a critical point where the effect becomes significant at a certain length of the axle polymer, which allowed us to conclude that the effect depends on component mobility and axle polymer length. Since the N-protection–deprotection method can be used, which was reported with an appropriate protecting group in our previous report, such amplification of a minor stimulus change to control the properties of the entire polymer is very interest-

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ing.[10] We believe the present work will lead to a better understating of the polyrotaxane structure, which can be directed toward future materials innovation.

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Keywords: macromolecular [2]rotaxanes · polymers · ring-opening polymerization · rotaxanes · supramolecular chemistry

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