Activation of Stable Polymeric Esters by Using Organo-Activated Acyl Transfer Reactions

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ABSTRACT: In this study, we succeeded in the *in situ* activation of nonactivated ester moieties embedded in polymer structures. Although poly(pentafluorophenyl methacrylate) (PPFPMA) can react with 2-ethylhexylamine at 50 °C in the presence of proton scavenger such as NEt_3, such conditions were not suitable for poly(phenyl methacrylate) (PPhMA). Nevertheless, the combination of organo-activating agents, namely 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) and 1,2,4-triazole (TZ) led to a facile conversion from ester to amide for PPhMA. The reaction between PPhMA and 2-ethylhexylaminewas conducted at 120 °C in the presence of one equivalent of TZ and three equivalents of DBU and yielded >99% ester conversion to afford corresponding polymethacrylamide derivatives as confirmed by FT-IR and ^{1}H NMR measurements. In addition, poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) and poly(methyl methacrylate) (PMMA) were also allowed to react with amines in the presence of the organo-activating agents with dramatically increased conversions (>70%). © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1353–1358

KEYWORDS: functionalization of polymers; organo-activated acyl transfer reactions; organo-catalysis; polyamides; poly (methacrylamides); post-polymerization modification; radical polymerization

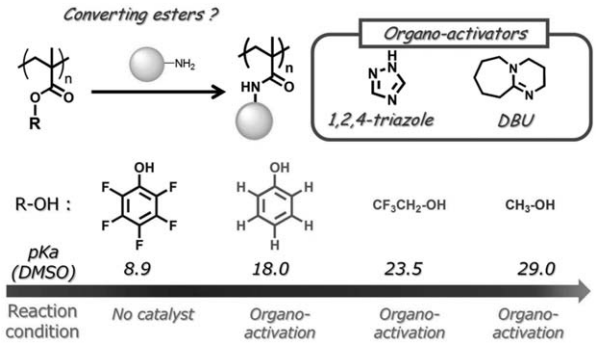
INTRODUCTION In a growing area of functional polymer science, polymers with readily clickable groups receive increasing attention because of their robust and reliable ability to yield functional materials such as bio-related polymers.[1–5] To expand the scope of clickable functional materials, many click type reactions have been utilized. This includes Cu(I) catalyzed[6] and metal-free[7] 1,3-dipolar cycloaddition reactions between organo-azides and acetylenes, as well as thiol-ene,[8,9] thiol-maleimide,[9] isocyanate-nucleophile,[10,11] and activated ester-amine[12] reactions, which all practically lead to quantitative conversions during the post-polymerization modification step.

Among the click reactions, polymeric activated esters have been appealing as facile candidates due to their reactions with amines. As boosted by an intensive effort on this research area, a wide range of activated esters is available. Polymers consisting of *N*-hydroxysuccinimide,[13] endo-*N*-Hydroxy-5-norborene-2,3-dicarboxyimide,[14] pentafluorophenoxy,[15] 2,3,5,6-tetrafluorophenoxy,[16] 4-nitrophenoxy,[17] 4-dimethylsulfoniumphenoxy salt,[18] and acetonoxime[19] based ester moieties have been described. All the aforementioned active ester moieties were revealed to show high reactivity toward amines and hence promoted various applications in bio-, medical-, and material-related areas.

Although these active esters provide a facile synthetic toolbox, the instinctive and inevitable drawback of polymeric activated esters is static reactivity toward nucleophiles. This is also true for the respective monomers featuring activated esters themselves. As a consequence, monomers featuring activated esters cannot be polymerized under nucleophilic conditions, such as anionic polymerization. In addition, the introduction of activated ester moieties can be expensive as compared with usual ester derivatives. Thus, *in situ* activation of nonactivated polymeric active esters should be a facile alternative synthetic protocol for the postmodification process based on activated ester chemistry. However, to the best of our knowledge, no studies on the *in situ* activation of polymeric nonactivated esters, for example PMMA, have been reported so far.

Hence, in this article, we describe (i) the evaluation of activating systems that allow polymeric nonactivated esters to react with amines and (ii) the optimization of these reaction conditions for the reactions between amines and polymeric nonactivated esters. To be precise, four kinds of polymers featuring esters with different leaving group abilities will be prepared. This includes poly(pentafluorophenyl methacrylate) (PPFPMA), poly(phenyl methacrylate) (PPhMA), poly (2,2,2-trifluoroethyl methacrylate) (PTFEMA), and poly

Ryohei Kakuchi and Kwanjira Wongsanoh contributed equally to this work.



SCHEME 1 Schematic overview of organo-activation of nonactivated polymethacrylate derivatives with different leaving group abilities.

(methyl methacrylate) (PMMA). The reactivity difference among the above-mentioned four polymers will be precisely studied (Scheme 1).

EXPERIMENTAL

Materials

Phenol was available from the Merck Co. and used without further purification. Methacryloyl chloride, 2,2,2-trifluoroethyl methacrylate (TFEMA), and 1,2,4-triazole were purchased from Sigma-Aldrich Chemicals Co., Inc., and used as received. All other chemicals were commercially available and used without further purification unless otherwise stated.

Instruments

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deuterated solvents and chemical shifts (δ) were given in ppm as solvent peak as internal standard. The size exclusion chromatography (SEC) was performed at room temperature in THF at a flow rate of 1.0 mL min^{-1}. The number-average molecular weight (M_n) and dispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. IR spectra were recorded on a Thermo Fisher Scientific Nicolet iS10 using an ATR unit.

Synthesis of Phenyl Methacrylate (PhMA)

The synthesis of PhMA was already reported[20] and the monomer was synthesized in a slightly modified route. Briefly, to a CH_2Cl_2 solution (30 mL) of phenol (10.0 g, 106 mmol) and triethylamine (12.4 g, 122 mmol), a CH_2Cl_2 solution (10 mL) of methacryloyl chloride (13.4 g, 128 mmol) was added at 0 °C dropwise for 30 min. The reaction mixture was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was filtered to remove a generated precipitate. The filtrate was rinsed with 1 mol L^{-1} HCl (aq), 1 mol L^{-1} K_2CO_3 (aq), and water. The organic phase was dried over $MgSO_4$. The obtained crude product was further purified by column chromatography (silica gel, eluent; ethyl acetate/petroleum ether = 1/80) to give phenyl methacrylate as transparent liquid. Yield: 14.5 g (89.3 mmol, 79.8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.01 (m, 5H), 6.39 (s, 1H), 5.78 (s, 1H), 2.10 (s, 3H). ^{1}H NMR data of the obtained monomer was in agreement with reported values.[20]

Typical Procedure for Radical Polymerization of Monomers

Synthesis of Poly(phenyl methacrylate) (PPhMA)

Phenyl methacrylate (11.1 g, 68.0 mmol) and AIBN (108 mg, 0.66 mmol) were dissolved in 25 mL of 1,4-dioxane. The solution was degassed with argon at room temperature for 15 min. After degassing, the reaction mixture was stirred at 80 °C overnight. The reaction mixture was cooled down and exposed to air in order to quench the polymerization. The solution was diluted with THF and poured into large excess of MeOH.

$$\text{Yield}: 10.0\ \text{g}\ (90.6\%).M_{\text{n,GPC}} = 13,800\ (\text{g mol}^{-1}).M_w/M_n = 2.75$$

Synthesis of Poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA)

$$\text{Yield}: 6.52\ \text{g}\ (65.2\%).M_{\text{n,GPC}} = 18,000\ (\text{g mol}^{-1}).M_w/M_n = 1.65.$$

Synthesis of poly(methyl methacrylate) (PMMA)

$$\text{Yield}: 7.62\ \text{g}\ (76.2\%).M_{\text{n,GPC}} = 12,500\ (\text{g mol}^{-1}).M_w/M_n = 1.65.$$

Typical Procedure for the Postmodification Reactions in the Presence of DBU and TZ Activators

To a DMSO-d_6/diglyme solution (0.5/0.5 mL) of PPhMA (260 mg, [ester] = 1.60 mmol), 1,2,4-triazole (110 mg, 1.60 mmol), and DBU (717 μL, 4.8 mmol), 2-ethylhexylamine (786 μL, 4.8 mmol) was added at room temperature. After the addition was complete, the reaction mixture was stirred at 120 °C for 24 h. After a portion of reaction mixture was separated to measure ^{1}H NMR spectrum in $CDCl_3$, the reaction mixture was poured into a large portion of CH_2Cl_2. The combined organic layer was washed with 1 mol L^{-1} HCl (aq) and Na_2CO_3 (aq). The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by reprecipitation in CH_2Cl_2/hexane to produce white powder. Yield: 190 mg (60.1%)

RESULTS AND DISCUSSIONS

Activation of Poly(phenyl methacrylate) in the Presence of Organo-Activator

In order to give a fundamental insight into the reactivity window of polymeric esters, a comparison between poly (pentafluorophenyl methacrylate) (PPFPMA), a known highly versatile activated ester polymer that is frequently utilized in polymer synthesis,[21–23] and poly(phenyl methacrylate) (PPhMA), was conducted because of their structural similarity and facile difference in the acidities of corresponding

TABLE 1 Organo-Activated Acyl-Transfer Reactions on Polymeric Esters[a]

Run	Polymer	[Ester]/[amine]$_0$/[TZ]$_0$/[DBU]$_0$	[Ester]$_0$ [b] (mol L^{-1})	Solvent	Time (h)	Temp. (°C)	Conv. of ester[c] (%)
1[d]	PPFPMA	1/2/0/2	0.8	THF	24	50	>99
2[d]	PPhMA	1/2/0/2	0.8	THF	24	50	4.1
3	PPhMA	1/3/1/3	0.8	DMSO-d_6/dgm (1/1, v/v)	24	120	>99
4	PPhMA	1/3/0/3	0.8	DMSO-d_6/dgm (1/1, v/v)	24	120	30.2
5	PPhMA	1/3/1/0	0.8	DMSO-d_6/dgm (1/1, v/v)	24	120	56.0
6	PTFEMA	1/3/1/3	0.8	DMSO-d_6/dgm (1/1, v/v)	24	120	59.9
7	PTFEMA	1/5/1/5	1.5	DMSO-d_6/dgm (1/1, v/v)	48	120	73.0
8	PMMA	1/5/1/5	1.5	DMSO-d_6/dgm (1/1, v/v)	48	120	72.6
9	PMMA	1/5/0/0	1.5	DMSO-d_6/dgm (1/1, v/v)	48	120	19.6

[a] Reactions were conducted with 2-ethylhexylamine (dgm; diglyme).
[b] The ester concentration was calculated ignoring amine components.
[c] Determined by ^{1}H NMR in $CDCl_3$ or DMSO-d_6 based on the assumption that ester moiety was converted to amide structure.
[d] NEt_3 was employed as a proton scavenger instead of DBU.

phenols (Table 1). To be precise, the pK_a value of pentafluorophenol in DMSO is determined to be 8.9[24] and that of phenol was determined to be 18.0,[25] which is supposed to induce a sufficient reactivity difference of the corresponding esters. Because postmodification reactions of nonactivated esters were expected to be conducted at fairly high temperature owing to their limited reactivity, 2-ethylhexylamine was selected as a model amine compound based on its high boiling point (169 °C under normal pressure). The reactions between the polymers and three equivalents of 2-ethylhexylamine were conducted in THF in the presence of NEt_3 as a proton scavenger. In agreement with the literature,[12] PPFPMA reacted with 2-ethylhexylamine in practically quantitative (>99%) conversion to afford the corresponding poly(*N*-2-ehtylhexyl methacrylamide). As expected, on the other hand, PPhMA showed very limited reactivity toward amines under the same reaction conditions (24 h, 50 °C) when compared with PPFPMA. To be precise, the ester conversion was determined to be only 4.1%. This clear difference in conversion of PPFPMA and PPhMA with 2-ethylhexylamine is mainly due to the difference in the leaving group ability of ester moieties and hence the reactivity of the ester.

Recently, Yang and Birman showed an elegant acyl transfer reaction system by using an organo catalytic system comprised of 1,2,4-triazole (TZ) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). To be precise, nonactivated esters, for example phenyl acetate, can be successfully employed as acyl donor toward amines in the presence of TZ/DBU organo catalysts.[26] In addition, they found that even methyl acetate, namely ultimate example of nonactivated esters, was allowed to react with amines in the presence of the TZ/DBU catalysts. The mechanism of TZ/DBU activated acyl transfer reactions can be described as follows. First, TZ is deprotonated by DBU to form a TZ anion. Second, the generated TZ anion reacts with the ester to form an activated carbonyl group as a reaction intermediate. Finally, the generated intermediate reacts with an amine yielding an amide.[26] This finding strongly implied that polymers featuring nonactivated esters should be able to be activated *in situ* and hence allowed to be reacted with amines in the presence of TZ and DBU mixed catalyst. Accordingly, we applied this organo-activating system comprising of TZ and DBU to the postmodification of nonactivated ester polymers (run 3, Table 1). Distinct cleavage of phenyl ester was observed for the reaction between PPhMA and 2-ethylhexylamine at 120 °C for 24 h in the presence of 1.0 equivalents of TZ and 3 equivalents of DBU. In a clear contrast to the reaction between PPhMA and 2-ethylhexylamine in the presence of NEt_3, the ester conversion reached under organo-activated conditions >99%. In order to give a direct evidence that the amidation reaction occurred at the phenyl ester, FT-IR measurement of the obtained polymers were performed. In the FT-IR spectrum of the obtained polymer after the reaction of PPhMA with 2-ethylhexylamine in the presence of TZ and DBU (Fig. 1), a distinct band at 1661 cm^{-1} owing to C=O stretching of amide group developed while the band at 1743 cm^{-1} owing to C=O stretching of phenyl ester group completely disappeared. In addition to the amide band at 1661 cm^{-1}, a clear band at 1716 cm^{-1} developed while the intensity was rather low as compared with the amide stretching.[27] This clearly indicated that intramolecular nucleophilic substitution reactions proceeded to afford imide formation in the polymer backbone to about 5% compared with amide structures as preliminarily estimated by IR measurements.[28] A SEC trace of the polymer after the organo-activated postpolymerization modification revealed that the reaction system did not involve any detectable decomposition or cross-linking of the polymer chains (Fig. 2). Thus, the amidation reaction of PPhMA indeed took place at carbonyl group, although the imide formation could not be ignored. In order to eliminate a possibility that DBU solely catalyzed the amidation reaction between PPhMA and 2-ethylhexylamine, control experiments were carried out (run 4 and 5, Table 1). In a clear contrast

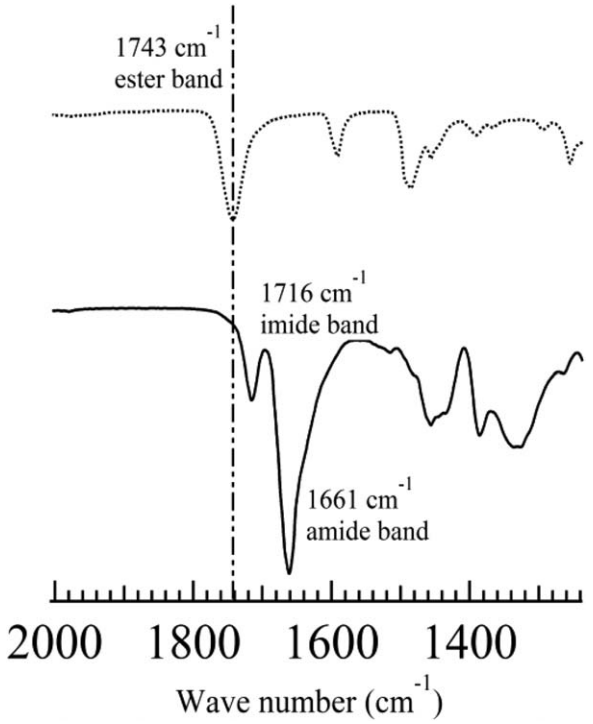


FIGURE 1 IR spectra of PPhMA before (upper) and after (lower) the reaction with 2-ethylhexylamine.

to the reaction in the presence of both DBU and TZ, only 56.0% conversion was achieved in the presence of only DBU. Furthermore, 30.2% conversion of ester linkage was observed for the reaction in the presence of only TZ. These control experiments clearly showed the importance of the combination of DBU and TZ as the organo-activating system.

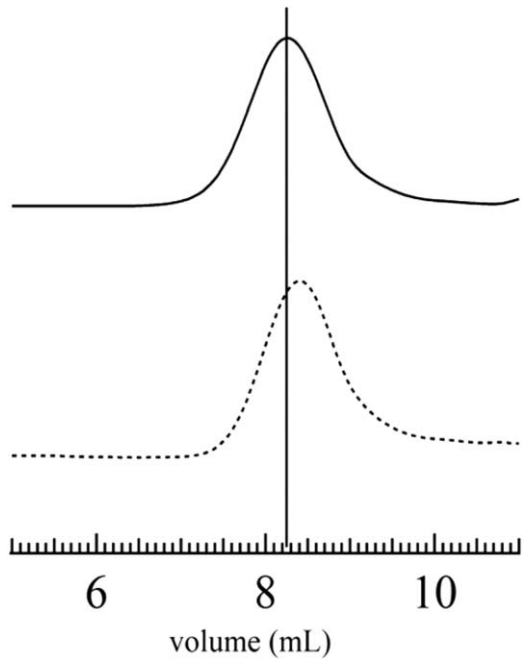


FIGURE 2 SEC traces of PPhMA (upper) and the obtained polymer (lower, Table 1, run 3) measured in THF.

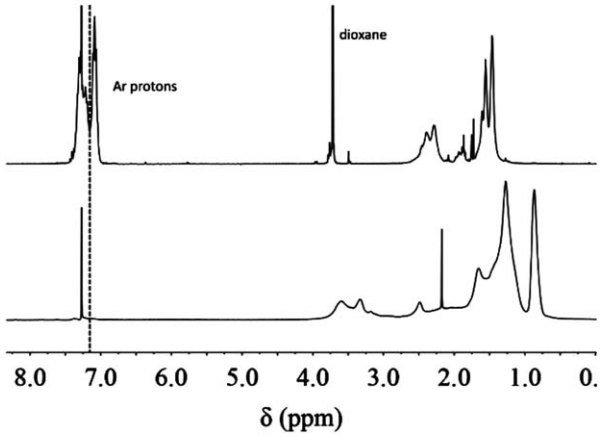


FIGURE 3 ^{1}H NMR spectra in $CDCl_3$ of PPhMA before (upper) and after (lower) the reaction with 2-ethylhexylamine.

In the ^{1}H NMR spectrum of PPhMA after reaction with 2-ethylhexylamine in the presence of TZ and DBU, distinct peak owing to 2-ethylhexyl protons was observed in the region from 0.7 to 1.2 ppm, which apparently indicated a successful installation of amines via amidation reaction (Fig. 3). Thus, the PPhMA was revealed to behave as a facile polymeric activated ester in the presence of DBU and TZ activating system.

Scope and Limitation of Activation of Polymeric Esters in the Presence of Organo-Activator

The phenyl ester shows a rather promising reactivity toward nucleophiles because of the efficient conjugation of benzene ring moiety. In order to give an insight into the scope and limitation of DBU and TZ catalytic system, polymeric esters with weaker leaving group ability than PPhMA were employed and reacted with amines. For this reason, 2,2,2-trifluoroethoxy ester was selected because 2,2,2-trifluoroethanol shows weaker acidity (pK_a = 23.5)[25] than phenol (pK_a = 18.0), which should theoretically result in a decrease of the leaving group ability of corresponding esters. First, poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA) was allowed to react with 2-ethylhexylamine under the same reaction condition as that for PPhMA (run 6, Table 1). Although the distinct ester cleavage was observed, the ester conversion was rather low. Hence, more harsh condition was applied (run 7, Table 1). As expected, release of 2,2,2-trifluoroethanol was enhanced to achieve 73.0% ester conversion. In order to give direct evidence that amidation reaction at 2,2,2-trifluoroethyl ester really occurred, FT-IR analysis of the obtained polymers were performed. In the FT-IR spectrum of the PTFEMA after reaction with 2-ethylhexylamine in the presence of TZ and DBU (Fig. 4), a distinct band at 1666 cm^{-1} owing to C=O stretching of amide group appeared while the band at 1744 cm^{-1} owing to C=O stretching of 2,2,2-trifluoroethyl ester group decreased in intensity. Thus, the amidation reaction of PTFEMA indeed took place at the carbonyl group. However, in a same manner to PPhMA, clear imidation reaction was observed, as confirmed by a sharp peak at 1717 cm^{-1} to about 9%

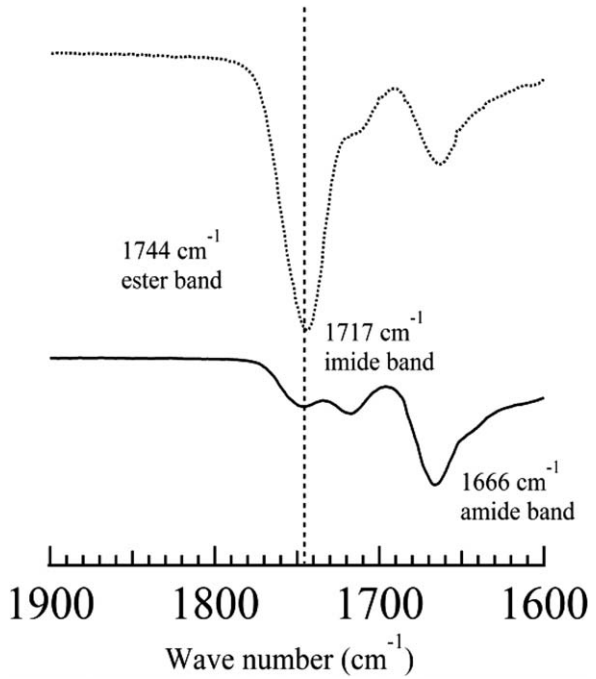


FIGURE 4 IR spectra of PTFEMA before (upper) and after (lower) the reaction with 2-ethylhexylamine.

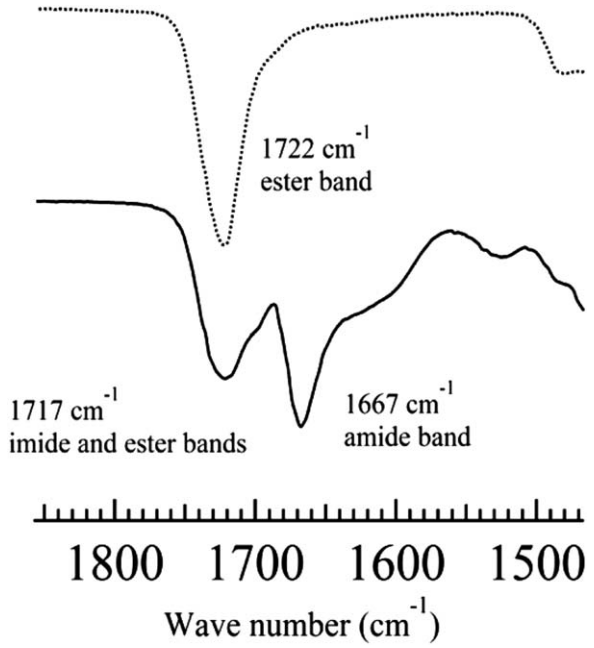


FIGURE 6 IR spectra of PMMA before (upper) and after (lower) the reaction with 2-ethylhexylamine.

compared with amide structures as preliminarily estimated by IR measurements. Thus, the degree of imidation was not enhanced as compared with the reaction of PPhMA. In addition, in the ^{1}H NMR spectrum of PTFEMA after reaction with 2-ethylhexylamine in the presence of TZ and DBU, a distinct peak owing to 2-ethylhexyl proton was observed in a region of 0.7 to 1.2 ppm, which clearly indicated a successful installation of amines via amidation reaction (Fig. 5). Thus, the PTFEMA was revealed to behave as a facile polymeric activated ester in the presence of DBU and TZ activating system although the ester conversion was lower than PPhMA.

As an ultimate goal of this study, a classical stable polymeric ester, namely PMMA, was employed as a precursor polymer. The leaving group ability of MeOH was rationally expected to be lower than that of CF_3CH_2OH because MeOH shows an even weaker acidity (pK_a = 29.0)[25] than CF_3CH_2OH (pK_a = 23.5)[25]. Thus, PMMA was allowed to react with 2-ethylhexyl amine under the same reaction conditions developed for PTFEMA (run 8, Table 1). Surprisingly, amidation reaction on PMMA took place with 72.6% ester conversion at 120 °C in the presence of large excess of organo-activator (run 8, Table 1). In order to give direct evidence that the amidation reaction really took place, FT-IR measurement of the obtained polymers were conducted. In the FT-IR spectrum of the PMMA after reaction with 2-ethylhexylamine in the presence of TZ and DBU (Fig. 6), a distinct band at 1667 cm^{-1} owing to C=O stretching of amide group developed while the band at 1722 cm^{-1} owing to C=O stretching of methyl ester group decreased in intensity. However, in a same manner to PPhMA and PTFEMA, clear imidation

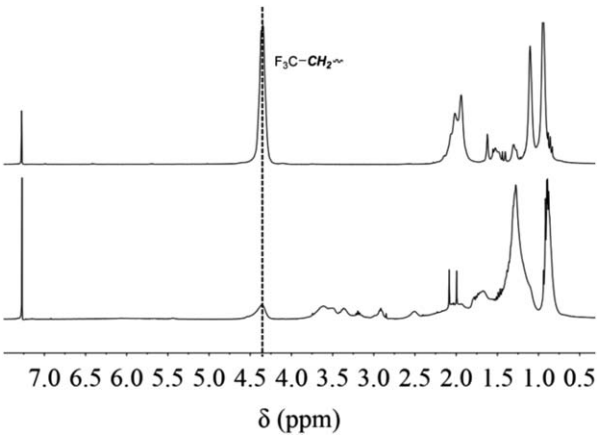


FIGURE 5 ^{1}H NMR spectra in $CDCl_3$ of PTFEMA before (upper) and after (lower) the reaction with 2-ethylhexylamine.

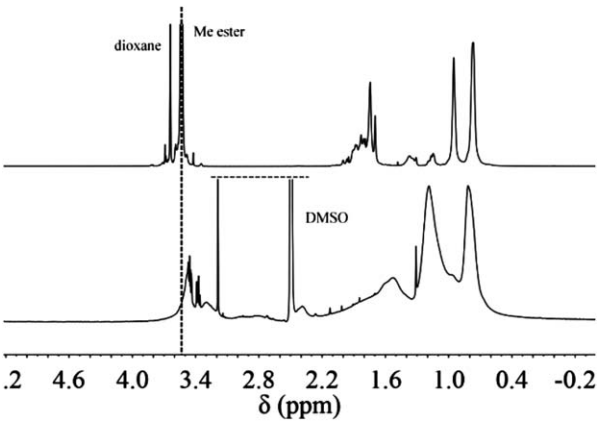


FIGURE 7 ^{1}H NMR spectra of PMMA before (upper in $CDCl_3$) and after (lower in DMSO-d_6 in the presence of TFA) the reaction with 2-ethylhexylamine.

reaction was observed to a certain degree, as confirmed by a sharp peak at 1717 cm^{-1}. In addition, in the ^1H NMR spectrum of PMMA after reaction with 2-ethylhexylamine in the presence of TZ and DBU, a distinct peak owing to 2-ethylhexyl protons was observed in the region from 0.7 to 1.2 ppm, which clearly showed a successful installation of amines via amidation reaction, demonstrating that the amidation reaction of PMMA indeed took place at carbonyl group (Fig. 7). Thus, the ultimately stable ester moieties in PMMA were revealed to behave as a facile polymeric activated ester in the presence of the DBU and TZ catalytic system. In a clear contrast to the reaction in the presence of organo-activators, only 19.6% of methyl esters of PMMA were consumed, showing a very limited reactivity of PMMA for the reaction in the absence of activators (Table 1, run 9).

This new chemical modification method should lead to new synthetic functionalization possibilities for the common polymer PMMA and thereby enhance the applications of PMMA within biomedical applications. In addition, synthesis of stereo-controlled polymethacrylamides is a long-lasting challenge in polymer synthesis and the herein presented synthetic methods opens a route to master this challenge. Starting from stereo-controlled polymethacrylates—whose synthetic protocols are rather established as compared with polymethacrylamides[29,30]—preparation of stereo-controlled polymethacrylamides should be straightforward and is currently under investigation.

CONCLUSIONS

In this study, we succeeded in the activation of nonactivated ester moieties embedded in polymer structures. Although PPFPMA was allowed to react with amines in the presence of proton scavenger such as NEt_3, PPhMA did not react with amines in the presence of NEt_3. However, the combination of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,2,4-triazole (TZ) yielded facile conversion from ester to amide for PPhMA with almost perfect conversion. In addition, under the same conditions as PPhMA, PTFEMA, and PMMA underwent amidation in the presence of the organo-activating agents, resulting in impressive degrees of conversion (>70%). To the best of our knowledge, this is the first report on using PMMA as a facile activatable ester precursor polymer for the synthesis of functionalized poly(methacrylamides) by using organo-activating method.

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