# Organometallic Chemistry

## Synthesis and reactivity of metal-containing monomers

## 52.* Synthesis and structure of Ti$^{IV}$-containing optically active monomers

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Optically active mixed alkoxy orthotitanates with general formula $Ti(OR^1)_2(OR^2)(OR^3)$ ($R^1$ = Et, Bu$^n$; $R^2$ = $CH_2CH_2OCOC(Me)=CH_2$; $R^3$ = menthyl, $CH(Me)CH_2Me$, $CH(Ph)CH(NHMe)Me$, $CH(C_9H_6N)(C_9H_{14}N)$) were obtained for the first time by transesterification. The Ti$^{IV}$ monomers synthesized were characterized by elemental analysis, ozonolysis, and $^1$H and $^{13}$C NMR and IR spectroscopy. Polymer products with optical activity were obtained by liquid phase radical copolymerization of Ti$^{IV}$-containing monomers.

**Key words:** mixed alkoxy orthotitanates, optically active monomers, transesterification, titanium-containing monomers, metal-containing polymers.

As early as 1954, A. N. Nesmeyanov and O. V. Nogina synthesized[2] and studied mixed esters of orthotitanic acid, including those based on allyl alcohol. The methods of preparation of aliphatic acyl and alkoxyl derivatives of biscyclopentadienyltitanium by the action of methacrylic acid and allyl alcohol on $(C_5H_5)_2TiCl_2$ were described in 1961.[3]

The mentioned ability of these Ti-containing products, in essence, metal-containing monomers (MCM) to form homopolymers and to be copolymerized with monomers of the traditional type, styrene or methyl methacrylate (MMA), has been confirmed experimentally.[4] The scope of Ti$^{IV}$-based monomers capable of polymerization has rapidly been extended.[5,6] Presently, for the synthesis of aliphatic alkyl orthotitanates of mixed type, the following reactions were studied in detail: direct action of alcohols on $TiCl_4$, interaction of alcohols (or sodium alcoholates) with alkoxytitanium halides (alkoxylation), substitution of alkoxyl groups in alkyl orthotitanates by aliphatic and other groups. The last method is named the transesterification reaction; it is often used for the preparation of mixed Ti$^{IV}$ monomers: in the cases where an aliphatic alcohol with a higher boiling temperature than that of the substituted alcohol is used for transesterification.[7]

$$Ti(OR^1)_4 + R^2OH \rightleftharpoons Ti(OR^1)_n(OR^2)_{4-n} + R^1OH \quad (1)$$

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[*] For Part 51, see Ref. 1.

[†] Deceased.

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The yielded alcohol can directly be removed from the reaction mixture during synthesis or distilled off as an azeotropic mixture with the solvent. Allyl, propargyl, and furfuryl alcohols, ethynyldimethylvinylcarbinol, and ethylene glycol monomethacrylate ($HOCH_2CH_2OCOC(Me)=CH_2$, EGM), containing high-reactivity multiple bonds, were used[8] as an unsaturated alcohol. The structure of the products formed ($Ti^{IV}$-containing monomers) was confirmed by different physicochemical methods (IR and NMR spectroscopies, ebullioscopy, and others). At the same time, even such a comparatively simple transesterification reaction as reaction (1) can be accompanied by several side transformations, the most substantial of which are disproportionation, complex formation of the yielded alcohol, oligomerization of the aliphatic ligand, a change in the degree of association of mixed alkyl orthotitanate, formation of alkoxo clusters, and others. Of course, optimization of conditions of this reaction makes it possible to reduce side processes to a minimum. Radical homopolymerization of these monomers[9] is non-trivial: the presence of the metal in the monomer molecule results in the electron density distribution on the growing center, different reactions of coordination of the initiating radical with monomers, participation of complex-bound radical species in chain termination reactions, and others.

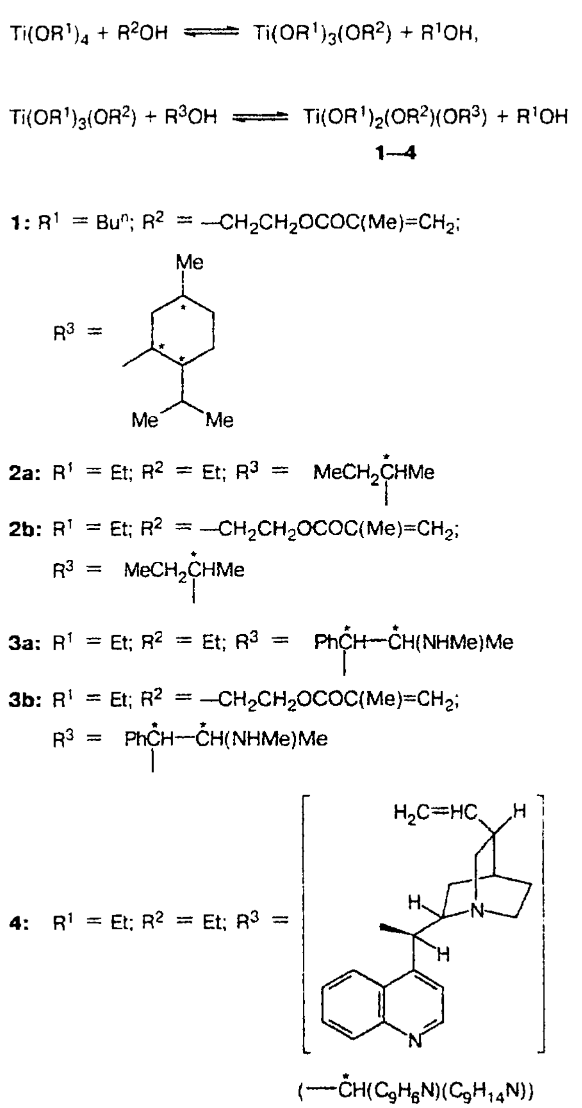
At the same time, on going from mixed alkyl orthotitanates, including groups of two different alcohols, to titanate containing three different groups, both synthetic and, especially, analytical difficulties increase sharply and, perhaps, due to this, similar products are not described in the literature. In particular, the introduction of an optically active alcohol residue, along with the alkoxy group capable of polymerization (of the EGM type), into the ligand environment of $Ti^{IV}$ would allow one to obtain optically active $Ti^{IV}$-containing monomers, and after their subsequent polymerization, optically active metallopolymers can be obtained, which are potential catalysts for enantioselective processes. The corresponding macromolecular $Ti^{IV}$ metal complexes, in which $Ti^{IV}$ catalyzes the reaction itself, and the presence of the asymmetric carbon atom in the alkoxy group stereochemically controls the process, can hypothetically be designed. This approach could be a heterogeneous variant of using homogeneous catalysts containing optically active modifying components,[10] as, *e.g.*, in the case of chiral polymeric Pd-containing catalysts of reduction of azlactone of acetamines of cinnamic acid.[11,12]

In this work, we attempted for the first time to synthesize monomers of this type, study their parameters, and reveal the possibility of their engagement in (co)polymerization processes.

## Results and Discussion

Tetrabutoxy- and tetraethoxytitanium, EGM as a ligand, and optically active alcohols, (−)-menthol, *sec*-butanol, and hydrochlorides of (−)-ephedrine and (−)-cinchonidine, were used as the starting reagents for the synthesis of mixed alkyl orthotitanates (Scheme 1).

**Scheme 1**



$$Ti(OR^1)_4 + R^2OH \rightleftharpoons Ti(OR^1)_3(OR^2) + R^1OH,$$

$$Ti(OR^1)_3(OR^2) + R^3OH \rightleftharpoons \underset{\mathbf{1-4}}{Ti(OR^1)_2(OR^2)(OR^3)} + R^1OH$$

**1**: $R^1$ = $Bu^n$; $R^2$ = $-CH_2CH_2OCOC(Me)=CH_2$;

$R^3$ =

**2a**: $R^1$ = Et; $R^2$ = Et; $R^3$ = $MeCH_2\overset{*}{C}HMe$

**2b**: $R^1$ = Et; $R^2$ = $-CH_2CH_2OCOC(Me)=CH_2$;

$R^3$ = $MeCH_2\overset{*}{C}HMe$

**3a**: $R^1$ = Et; $R^2$ = Et; $R^3$ = $Ph\overset{*}{C}H-\overset{*}{C}H(NHMe)Me$

**3b**: $R^1$ = Et; $R^2$ = $-CH_2CH_2OCOC(Me)=CH_2$;

$R^3$ = $Ph\overset{*}{C}H-\overset{*}{C}H(NHMe)Me$

**4**: $R^1$ = Et; $R^2$ = Et; $R^3$ =

($-\overset{*}{C}H(C_9H_6N)(C_9H_{14}N)$)

As discussed above, transesterification is a convenient method for the synthesis of $Ti^{IV}$-containing monomers of the type under consideration. According to reaction (1), low-boiling butanol and ethanol that formed during transesterification were distilled off in the form of an azeotropic mixture with a solvent, thus inducing the shift of equilibrium toward the target product, and the process was qualitatively and quantitatively monitored by chromatographic analysis of the azeotropic mixture. For example, in the synthesis of compound **1**, the main portion of the azeotropic mixture was distilled

**Table 1.** Elemental analysis data for $Ti^{IV}$-containing monomers

| Monomer | Found/Calculated (%) C | H | Ti | Molecular formula |
|---|---|---|---|---|
| **1***  | 58.9<br>60.22 | 8.9<br>9.69 | 9.60<br>10.03 | $C_{24}H_{46}O_6Ti$ |
| **2a** | 45.9<br>46.85 | 8.59<br>9.44 | 17.6<br>18.69 | $C_{10}H_{24}O_4Ti$ |
| **2b** | 48.3<br>49.39 | 7.50<br>8.30 | 14.3<br>14.10 | $C_{14}H_{28}O_6Ti$ |
| **3a** | 54.7<br>55.34 | 7.82<br>8.42 | 13.1<br>13.79 | $C_{16}H_{29}NO_4Ti$ |
| **3b** | 55.1<br>55.69 | 6.90<br>7.71 | 10.37<br>11.10 | $C_{20}H_{33}NO_6Ti$ |
| **4** | 62.8<br>63.02 | 6.8<br>7.62 | 11.3<br>10.05 | $C_{25}H_{36}N_2O_4Ti$ |

* Content of double bonds (mole per mole of monomer): 1.11±0.07.

off at 75 °C and contained 11.3 wt.% *n*-butanol, although in mixtures that were distilled off during the reaction the content of *n*-butanol was 5.98—13.10%, and the interval of their boiling temperatures was 68—78 °C. Since polymerization of MCM could occur during introduction of an unsaturated ligand into mixed titanium alkoxide and, especially, during distillation of the azeotropic mixture, for the synthesis of compounds **2**—**4**, we primarily substituted one alkoxy group in $Ti(OEt)_4$ by the residue of the optically active alcohol (reaction (2)), and then, at the second stage, transesterification involving an unsaturated alcohol was carried out (reaction (3)).

$$Ti(OEt)_4 + R^3OH \rightleftharpoons Ti(OEt)_3(OR^3) + EtOH \qquad (2)$$

$$Ti(OEt)_3(OR^3) + R^2OH \rightleftharpoons$$
$$\rightleftharpoons Ti(OEt)_2(OR^3)(OR^2) + EtOH \qquad (3)$$

However, during this process, as, *e.g.*, in the case of compounds **2b**, a high-boiling aliphatic alcohol can substitute both the ethoxy group and the optically active $Bu^s$ group. According to the chromatographic analysis data, the formation of ethanol and *sec*-butanol is observed during the reaction of $Ti(OEt)_3[OCH(Me)CH_2Me]$ with $R^2OH$ at 50 °C, which indicates the substitution of alkoxy groups of both types. This undesirable substitution was prevented, on the one hand, by the replacement of $Ti(OBu^n)_4$ by $Ti(OEt)_4$ and, on the other hand, by the reaction being carried out at a temperature close to room temperature followed by distillation of the azeotropic mixture *in vacuo*.

Products **1** and **2** are yellowish viscous liquids, and compounds **3** and **4** are solids soluble in organic solvents. The elemental analysis data for the $Ti^{IV}$ monomers synthesized are presented in Table 1.

We compared the optical activity of the $Ti^{IV}$-containing products obtained and initial optically active alcohols. As can be seen from the data in Table 2, the optical properties of $Ti^{IV}$ monomers are comparable with the optical activity of the initial alcohols. The values of optical rotation for compounds **2a**,**b** and **3a**,**b** presented in Table 2 have, most likely, the qualitative character, which confirms that the orthotitanate and related polymer contain the corresponding chiral alcohol. Unlike monomer **1** and its polymer, the optical rotation values for these products were determined in the DMSO—HCl(conc.) mixture, in which the polymers obtained from compounds **2a**,**b** and **3a**,**b** are soluble. However, hydrolysis of $Ti(OR)_n(OR)_{4-n}$ fragments occurs in this mixture. Presently, it is impossible to take into account the influence of hydrolysis on the optical activity (including the possible racemization of the fragments), because this requires a special study.

The structures of the $Ti^{IV}$-containing products synthesized and previously described mono-substituted alkoxy derivatives of titanium[8] were studied by spectroscopy. For example, the $^{13}C$ NMR spectrum of com-

**Table 2.** Optical rotation of ligands ($[\alpha]^{20}$) and related $Ti^{IV}$-containing monomers ($[\alpha_M]^{20}$)

| Monomer | $[\alpha]^{20}$ ($[\alpha_M]^{20}$) 589 nm | 578 nm | 546 nm | 436 nm | 365 nm |
|---|---|---|---|---|---|
| **1** | −46.05 (−220.7)[a] | — | — | — | — |
| | −35.5 (−170.2)[b] | −37.4 (−179.2)[b] | −42.7 (−204.3)[b] | −74.9 (−358.2)[b] | — |
| (−)-Menthol | −38.6 (−60.2)[a] | — | — | — | — |
| **2a** [c] | −9.2 (−23.5) | −10.4 (−26.6) | −14.3 (−36.6) | −24.4 (−62.5) | −34.2 (−87.5) |
| **2b** [d] | −3.2 (−10.9) | −4.3 (−14.6) | −7.4 (−25.2) | −17.1 (−58.1) | −28.2 (−95.9) |
| $Bu^sOH$ [e] | −29.1 (−21.5) | −31.3 (−23.2) | −35.3 (−26.1) | −57.4 (−42.5) | −94.1 (−69.6) |
| **3a** [f] | −20.1 (−69.7) | −20.7 (−71.8) | −23.9 (−82.9) | −40.8 (−141.6) | — |
| **3b** [g] | −8.9 (−38.4) | −9.2 (−39.6) | −10.6 (−45.7) | −18.4 (−79.3) | — |
| Ephedrine [h] | −34.2 (−68.9) | −36.1 (−72.7) | −41.0 (−82.6) | −68.9 (−138.8) | — |
| **4** [i] | +50.9 (+242.3) | +82.8 (+394.1) | +209.8 (+998.6) | — | — |

[a] *c* 3, hexane. [b] *c* 1.3, benzene. [c] *c* 3.4, DMSO—HCl(conc.), 1 : 1. [d] *c* 2.8, DMSO—HCl(conc.), 1 : 1. [e] *c* 0.8, DMSO—HCl(conc.), 1 : 1. [f] *c* 1.40, DMSO—HCl(conc.), 1 : 1. [g] *c* 1.5, DMSO—HCl(conc.), 1 : 1. [h] *c* 1.4, DMSO—HCl(conc.), 1 : 1. [i] *c* 1.6, benzene.

pound **1** has parameters close to the spectral parameters of the starting (−)-menthol. The chemical shifts of asymmetric carbon atoms are 76.4 (71.8), 52.3 (51.0), and 32.7 (32.5) ppm (δ for (−)-menthol are presented in parentheses).

Physicochemical studies show that exchange reaction (2) proceeds with quantitative substitution of the initial alkoxy group by the chiral group, and the initial components are absent in the final products. Probably, disproportionation processes are completely suppressed or occur with low rates, because the spectral parameters of the products do not change in time. The $^1$H and $^{13}$C NMR spectra of alkoxy orthotitanates under study contain no broadened signals, and their simplicity, "homogeneity" confirm the individual character of the compounds synthesized.

To obtain the corresponding metallopolymers, we studied reactions of homopolymerization and copolymerization of the Ti-containing monomers synthesized. The homopolymerization of Ti$^{IV}$ monomer **1** results in the formation of a polymeric product ($\bar{M}_n$ = 30800) with $[\alpha]_D^{20}$ = −6° (*c* 0.58, $CHCl_3$—MeOH, 1 : 1). The decrease in the specific rotation as compared with that of the monomeric analog (for **1**, $[\alpha]_D^{20}$ = −46.05°, see Table 2) can be related to the formation during polymerization of new asymmetrical centers differing in the direction of rotation of the polarized light plane and in the effect of the solvent nature. Copolymers **1** with 4-vinylpyridine (4-VinPy) (the molar fraction of **1** is 4%) and MMA (the molar fraction of **1** is 1.5%) ($\bar{M}_n$ = 60000—63000) with a specific rotation of −0.8° (*c* 1.4, $CHCl_3$—MeOH, 1 : 1) were obtained. For copolymer **2b** with styrene (the molar fraction of **2b** is 4.9%), $[\alpha]_D^{20}$ is −0.041° (*c* 6.2, DMSO—HCl(conc.), 1 : 1). Low values of specific rotation are probably related to a low content of MCM units in the copolymer chain.

Thus, a method of synthesis of optically active metal-containing monomers has been developed, and unsaturated alkoxy derivatives of Ti$^{IV}$ with optically active properties have been synthesized and characterized for the first time. It can be assumed that this approach will be fruitful for synthesis of the corresponding monomers based on $(C_5H_5)_2TiCl_2$ (as described for amide cyclopentadienyl complexes Ti$^{IV}$ [13] and chiral carboxylate molybdocenes[14]) and alkoxy derivatives of other metals. For example, we have previously described[15] MCM based on alkoxy derivatives of V$^V$ and shown[16] their ability for homo- and copolymerization with styrene, MMA, and acrylonitrile. Probably, compounds of the $VO(OR^1)(OR^2)(OR^3)$ type with chiral ligands and the corresponding related metallopolymers can be synthesized by transesterification. Our further reports will be devoted to the synthesis and structural study of these compounds and the catalytic properties of the products obtained in reactions of asymmetrical synthesis.

## Experimental

Tetrabutoxytitanium ($Ti(OBu^n)_4$) was distilled *in vacuo* (b.p. 134—136 °C (0.5—1 Torr)). Admixtures of dimethacrylates in ethylene glycol monomethacrylate (EGM) were removed by extraction from the aqueous solution with petroleum ether, and purified EGM was distilled *in vacuo* (b.p. 52 °C (1 Torr)). Solvents were purified by standard procedures; styrene, MMA, and 4-VinPy were used freshly distilled. (−)-Menthol (m.p. 42.5 °C, $[\alpha]_D^{20}$ = −38.6° (*c* 3, hexane)) and hydrochlorides of (3*R*,4*S*,8*S*,9*R*)-(−)-cinchonidine (m.p. 202 °C, $[\alpha]_D^{20}$ = −109.2° (*c* 1.5, EtOH)) and (1*S*,2*R*)-(−)-ephedrine (m.p. 220 °C, $[\alpha]_D^{20}$ = −34.2° (*c* 1.4, DMSO—HCl(conc.), 1 : 1)) were used without additional purification; (*R*)-(−)-Bu$^s$OH was isolated as brucine phthalate followed by treatment with HCl and distillation (b.p. 100 °C, $[\alpha]_D^{20}$ = −29.1° (*c* 0.8, DMSO—HCl(conc.), 1 : 1)); $(Bu^nO)_3Ti[OCH_2CH_2OCOC(Me){=}CH_2]$ was prepared by the previously described procedure.[8] IR spectra were recorded on a Perkin—Elmer 325 spectrometer in a benzene solution in sealed KBr cells. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC-200 spectrometer in $C_6D_6$. GLC analysis was carried out on an LKhM-8MD chromatograph (Chezasorb AW as the stationary phase, impregnated 15% Carbowax-1500, argon as the carrier gas). Optical rotation was measured on a JASCO DIP-360 spectropolarimeter. Elemental analysis was performed by the organic microanalysis and atomic-adsorption nonflame methods on a Saturn instrument. The content of double bonds was determined by ozonolysis on an ADS-4M analyzer of double bonds. The number-average molecular weight ($\bar{M}_n$) of copolymers was measured in DMF on a Hewlett-Packard 502 membrane osmometer.

**Synthesis of [(1*R*,2*S*,5*R*)-(−)-menthoxy](methacryloxyethoxy)(di-1-butoxy)titanium, $(Bu^nO)_2Ti[OCH_2CH_2O{-}COC(Me){=}CH_2][OCHCH_2CH(Me)CH_2CH_2CH(Pr^i)$-*cyclo*] (1).** (−)-Menthol (3.94 g, 0.025 mol) in benzene (10 mL) was added to a solution of (β-methacryloxyethoxy)tributoxytitanium (10 g, 0.025 mol) in benzene (15 mL). The reaction was carried out for 2 h with simultaneous distillation of butanol that formed in an azeotropic mixture with benzene. After the reaction mixture was distilled *in vacuo*, product **1** (10.86 g, 90% of the theoretical yield) was obtained as a yellow transparent viscous liquid. IR, ν/cm$^{-1}$: 1639 (C=C); 1719 (C=O); 1384 ($CMe_2$); 1297, 1322 (CCCO). $^1$H NMR (200 MHz), δ: 0.98 (m, 3 H, $CH_3$, menthyl); 2.03 (m, 3 H, $CH_3$); 2.30 (m, 6 H, 2 $CH_2$, menthyl); 1.65—1.95 (m, 2 $CH_2$, menthyl); 4.19 (t, 1 H, CHO, *J* = 12.8 Hz); 5.69 (s, 1 H, $CH_2$=); 6.52 (s, 1 H, $CH_2$=). $^{13}$C NMR (50 MHz), δ: 16.9 ($CH_3$); 18.9 ($CH_2$); 21.7, 32.7, 52.3 (CH, menthyl); 76.3 (OCH, menthyl); 35.7, 46.9 ($CH_2$, menthyl); 64.9 ($CH_2$); 126.2 ($CH_2$=); 138.0 (>C=).

**Synthesis of (2-butoxy)triethoxytitanium, $(EtO)_3Ti(OBu^s)$ (2a).** Bu$^s$OH (1.36 g, 0.018 mol) in benzene (30 mL) was added to $Ti(OEt)_4$ (4.2 g, 0.018 mol) in benzene (25 mL) with simultaneous distillation of a benzene—EtOH azeotropic mixture. Benzene (40 mL) was added during the reaction. According to the chromatographic analysis data, the yield of EtOH was 95%. Monomer **2a** was obtained in 97% yield (4.5 g).

**Synthesis of (methacryloxyethoxy)(2-butoxy)triethoxytitanium, $(EtO)_2Ti[OCH_2CH_2OCOC(Me){=}CH_2](OBu^s)$ (2b).** Ethylene glycol monomethacrylate (2 g, 0.015 mol) in benzene (40 mL) was added to a solution of $(EtO)_3Ti(OBu^s)$ (3.8 g, 0.015 mol) in benzene (10 mL). The reaction mixture was kept at 10 °C for 1 h, and then a mixture of benzene with EtOH that formed was removed *in vacuo*. Monomer **2b** was obtained in 96% yield (4.9 g).

**Synthesis of [(1*R*,2*S*)-(−)-α-(1-methylaminoethyl)benzoxy]triethoxytitanium, $(\mathrm{EtO})_3\mathrm{Ti}[\mathrm{OCH(Ph)CH(NHMe)Me}]$ (3a).** (−)-Ephedrine hydrochloride (1.2 g, 0.005 mol) was added to a solution of $\mathrm{Ti(OEt)_4}$ (1.17 g, 0.005 mol) in benzene (45 mL). An azeotropic mixture of benzene with EtOH that formed was distilled off during chromatographic monitoring (b.p. 75 °C). Monomer **3a** was obtained in 86% yield (1.5 g).

**Synthesis of [(1*R*,2*S*)-(−)-α-(1-methylaminoethyl)benzoxy](methacryloxyethoxy)diethoxytitanium, $(\mathrm{EtO})_2\mathrm{Ti}[\mathrm{OCH_2CH_2OCOC(Me){=}CH_2}][\mathrm{OCH(Ph)CH(NHMe)Me}]$ (3b).** Ethylene glycol monomethacrylate (0.51 g, 0.0039 mol) in benzene (10 mL) was added to a solution of compound **3a** (1.5 g, 0.0039 mol) in benzene (20 mL). The conditions of the reaction and isolation of the product were the same as those in the synthesis of compound **2b**. Monomer **3b** was obtained in 93% yield (1.6 g).

**Synthesis of [(3*R*,4*S*,8*S*,9*R*)-(−)-cinchonidoxy]triethoxytitanium, $(\mathrm{EtO})_3\mathrm{Ti}[\mathrm{OCH(C_9H_6N)(C_9H_{14}N)}]$ (4).** (−)-Cinchonidine hydrochloride (0.99 g, 0.0034 mol) was added to a solution of $\mathrm{Ti(OEt)_4}$ (0.77 g, 0.0034 mol) in benzene (30 mL). The conditions of the reaction and isolation of the product were the same as those in the synthesis of compound **2b**. Monomer **4** was obtained in 97% yield (1.57 g).

**Homopolymer 1.** Monomer (2 g, 0.004 mol), azobis(isobutyronitrile) (AIBN) (0.04 g), and heptane (30 mL) were placed in a glass tube. The tube with the reaction mixture was degassed, sealed *in vacuo*, and placed in a thermostat at 70 °C. The duration of polymerization was 7 h. The product was isolated by filtration, washed with heptane, and dried *in vacuo* at 40 °C. The yield of the polymer was 0.8 g (40%).

**Copolymer 1 with 4-vinylpyridine.** Monomer **1** (0.5 g, 0.001 mol), 4-VinPy (2.43 g, 0.02 mol), AIBN (0.05 g), and heptane (20 mL) were placed in a glass tube. The tube with the reaction mixture was degassed, sealed *in vacuo*, and placed in a thermostat at 70 °C. The duration of polymerization was 5 h. The yield of the polymer was 2.33 g (79%).

**Copolymer 1 with MMA.** The initial reaction mixture contained monomer **1** (1 g, 0.002 mol), MMA (1.87 g, 0.02 mol), AIBN (0.06 g), and heptane (30 mL). Conditions of copolymerization and isolation of the product were the same as those for the copolymer with 4-VinPy. The yield of the polymer was 1.81 g (63%).

**Copolymer 2b with styrene.** The initial reaction mixture contained monomer **2b** (4.8 g, 0.014 mol), styrene (1.5 g, 0.014 mol), AIBN (0.063 g), and benzene (50 mL). Conditions of copolymerization and isolation of the product were the same as those for the copolymer with 4-VinPy. The yield of the polymer was 0.85 g (13.5%). The copolymer is soluble in a DMSO—HCl(conc.) (1 : 1, v/v) mixture.

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