

Linear-Dendritic Copolymers as Nanocatalysts

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ABSTRACT: Functionalized poly(ethylene glycol) (PEG) containing four chloride end functional groups (PEG-Cl₄) was synthesized through reaction between cyanuric chloride and PEG-(OH)₂. Chloride end functional groups of PEG-Cl₄ were able to initiate the ring opening polymerization of 2-ethyl-2-oxazoline and star copolymers containing a PEG core, and poly(2-ethyl-2-oxazoline) (POX) arms were obtained. Polymerization was quenched using diethanolamine, and star copolymers containing hydroxyl end functional groups (PEG-POX-OH) were obtained. ϵ -Caprolactone was then polymerized using the hydroxyl end

functional groups of star copolymers and amphiphilic linear-dendritic copolymers containing PEG and POX, and poly(caprolactone) (PCL) blocks were synthesized. Linear-dendritic copolymers were able to load the organic and inorganic guest molecules. Application of host-guest systems such as nanocatalyst for Heck chemical reaction was also investigated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2072–2080, 2009

Key words: nanocatalyst; poly(oxazoline); linear-dendritic; Heck reaction; amphiphilic

INTRODUCTION

Dendrimers possessing unique properties and microstructures have aroused interest in different scientific areas.^{1–5} However, the long time and high cost synthesis of perfect dendrimers avoids their production in the high scale.

Linear-dendritic, dendrigraft, and dendrimer-like star macromolecules are different types of dendritic macromolecules whose structure is not as controllable as perfect dendrimers, but their synthesis is easier than that for perfect dendrimers; hence they are promising materials to overcome the mentioned drawback of perfect dendrimers.

Dendrigraft and dendrimer-like star macromolecules are highly branched macromolecules introduced simultaneously in 1991 as Comb-burst polymers by Tomalia et al.⁶ and as arborescent polymers by Gauthier and Möller.⁷ Variety dendrigrafts were synthesized and investigated by Gauthier et. al in recent years.^{8–21}

Synthesis, solution behavior, and transport properties of amphiphilic dendrigrafts also were investigated by Deffieux et al.^{22–26}

Linear-dendritic copolymers are hybrid structures that combine two types (linear and dendritic) of macromolecular architectures. In the past several

years, a significant number of reports on the preparation of such hybrid copolymers have appeared in the literature.^{27–40}

Recently, the synthesis and application of variety of linear-dendritic macromolecules containing a linear core and different dendrons have been reported by Gitsov and Hammond.^{27–43} ABA linear-dendritic copolymers and linear-dendritic macromolecules containing a dendritic core and linear arms were also synthesized by our research group.^{44–48} The host-guest properties, solution behaviors, and their application as drug delivery agents were also investigated.^{44–50} Synthesis of the functionalized PEG containing cyanuric chloride segments was reported by our research group for the first time, and it was used for preparation of the ABA-type linear-dendritic copolymers.^{45,46} Due to the high reactivity of chloride functional groups of cyanuric chloride, we considered it as a new initiator for ring opening polymerization of oxazoline monomers. Based on this idea, in this work we used the functionalized PEG containing end cyanuric chloride segments for ring opening polymerization of 2-ethyl-2-oxazoline. Polymerization of 2-ethyl-2-oxazoline, using this macroinitiator and quenching of polymerization using diethanolamine, was led to star copolymers containing a PEG core and POX arms with hydroxyl end functional groups. Hydroxyl end functional groups of POX arms were then used for ring opening polymerization of ϵ -caprolactone, and amphiphilic linear-dendritic copolymers were obtained. Loading of Congo red and PdCl₂ by linear-dendritic copolymers was also investigated. Finally, the catalytic activity

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of linear-dendritic copolymers containing PdCl₂ toward the Heck chemical reaction was investigated.

EXPERIMENTAL

Characterization

¹H NMR spectra were recorded in CDCl₃ solution on a Bruker (Germany) DRX 400 (400 MHz) apparatus with the solvent proton signal for reference. ¹³C-NMR spectra were recorded at 125.721 MHz on the same instrument, using the solvent carbon signal as a reference. The number-average molecular weights of the polymers were calculated from the ¹H-NMR data. IR measurements were performed using a Nicolet 320 FTIR. Dynamic light scattering experiments were performed with commercially available equipment (Zetasizer Nano from Malvern) [United Kingdom] using a 4-mW He-Ne laser (633 nm wavelength) with a fixed detector angle of 173°. The molecular weight distributions were determined by size exclusion chromatography (SEC) (Agilent 1100) using a PSS GRAL 100 Å column connected to a differential refractometer, with an RI detector with chloroform as the mobile phase at 25°C. Poly(styrene) standard samples were used for calibration. GC-Mass experiments were recorded using a Shimadzu GCMS-QP 505 A with DB5 column.

Materials

Cyanuric chloride, *O*-anisidine, poly(ethylene glycol) (*M_n* = 1000), 2-ethyl-2-oxazoline, diethanolamine, iodobenzene, ethyl acrylate, and PdCl₂ were purchased from Merck.

Preparation of PEG-Cl₄

PEG was functionalized using cyanuric chloride according to reported procedure in the literature.^{45,46} Briefly, PEG was dissolved in a solution of sodium hydroxide in water, and it was then added to a solution of cyanuric chloride in dichloromethane at 0°C. The mixture was stirred for 2 h at room temperature and it was refluxed for 6 h. It was then filtrated, and the product was precipitated in diethyl ether.

Synthesis of star copolymers containing hydroxyl end functional groups (PEG-POX-OH)

0.2 g (0.15 mmol) of functionalized PEG (PEG-Cl₄) was dissolved in 20 mL of dried acetonitrile. 0.63 mL (6.2 mmol) of 2-ethyl-2-oxazoline was added to this solution, and it was stirred at 120°C for 2 days. The temperature of reaction was reduced to 60°C, and diethanolamine (excess) was added to the solution; it was then stirred for 2 h. The solution was filtered, and solvent was evaporated. Residue was then dissolved in methanol, and the product was precipitated in diethyl ether as a yellow viscous compound in 80% yield.

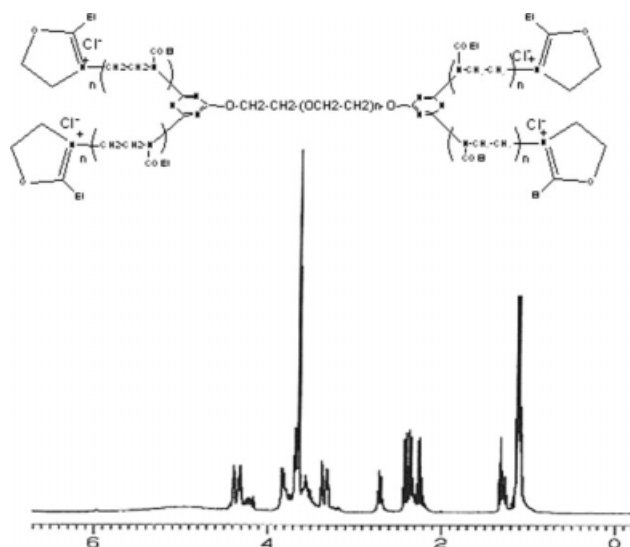


Figure 1 ¹H-NMR spectra of PEG-POX containing living POX arms.

Synthesis of star copolymers containing end aromatic groups

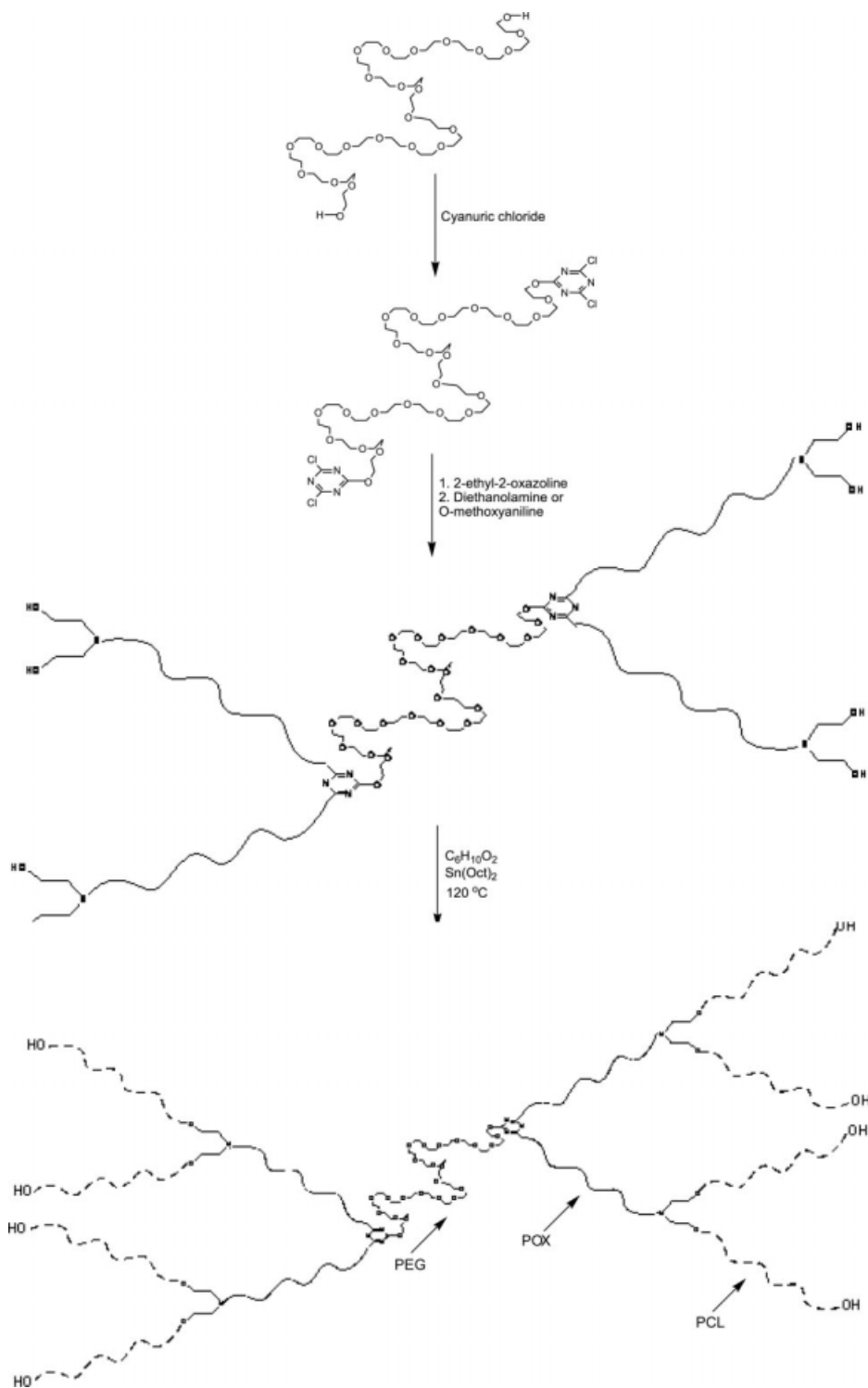
The procedure for synthesis of star copolymers containing end aromatic groups was similar to that for their analogues containing hydroxyl end functional groups, but here the quenching was carried out using *O*-anisidine. Purified product was obtained as a brown solid compound in 70% yield.

Synthesis of linear-dendritic amphiphilic copolymers

0.2 g of star copolymer containing PEG core and POX arms and end hydroxyl or aromatic groups was added to a polymerization ampule equipped with a magnetic stirrer and vacuum inlet. 1 mL of toluene solution of Sn(Oct)₂ (1 × 10⁻³ M) was added to this polymerization ampule, and solvent was evaporated under vacuum at 60°C for 30 min. 1 mL of ε-caprolactone was then added to the polymerization ampule, and it was left under vacuum at 60°C for 1 h. The polymerization ampule was sealed under vacuum, and the mixture was stirred at 120°C for 6 h. Then ampule was cooled, and the contents were dissolved in chloroform. The solution was filtrated, and the product was precipitated in diethyl ether. The yield of the reaction was 80%.

Loading of congo red

0.2 g of copolymer was dissolved in 10 mL chloroform, and it was stirred for 1 h. Then Congo red (excess) was added to this solution, and the mixture was stirred for 2 h at room temperature. The mixture was filtered and the solution was centrifuged; clear solution was decanted for UV experiments.



Scheme 1 Synthesis of linear-dendritic copolymers.

Loading of Pd^{+2} by linear-dendritic copolymers

Linear-dendritic copolymers were dissolved in distilled water, and the solution was stirred for 30 min. Then $PdCl_2$ was added to the solution, and it was stirred for 24 h. The solvent was evaporated and the compound was dissolved in dichloromethane, and the purified product was precipitated in cyclohexane.

Linear-dendritic copolymer/ Pd^{+2} as nanocatalysts

Iodobenzene (29 mmol, 6 mL) was added to 50 mL dimethyl formamide and it was stirred for 10 min; ethyl acrylate (60 mmol, 6 mL) was then added to the solution, and it was stirred for 5 min. Linear-dendritic copolymer/ pd^{+2} (0.2 g) and triethylamine (9.9 mmol, 1 mL) were also added to the solution,

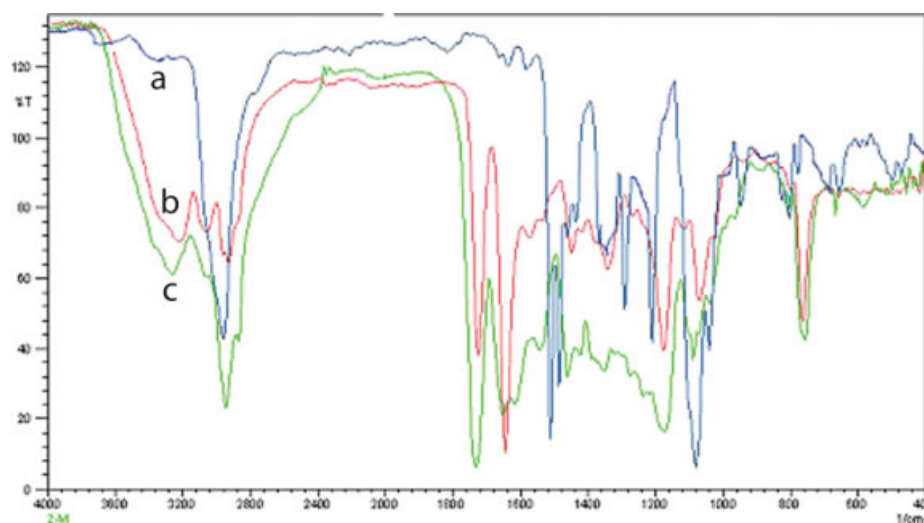


Figure 2 IR spectra of (a) PEG-Cl₄, (b) PEG-POX, and (c) PEG-POX-PCL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and the mixture was stirred at room temperature. Reaction was followed by GC-Mass.

RESULTS AND DISCUSSION

Poly(ethylene glycol) was functionalized using cyanuric chloride according to the reported procedure in our previous papers. The end cyanuric chloride segments of PEG-Cl₄ were able to initiate the ring opening polymerization of 2-ethyl-2-oxazoline monomer and star copolymers containing PEG core, and POX arms were obtained. End cationic monomers of POX arms were active for several days, and they were able to react with nucleophiles. Quenching the polymerization using different nucleophiles led to copolymers with different properties. Figure 1 shows the ¹H-NMR spectra of star copolymer containing living POX arms. Signals of POX arms appeared at 3.5, 2.4–2.2, and 1.2–1.1 ppm for -CH₂-N-, -CO-CH₂- and methyl groups, respectively. Signals at 4.2–4.9 ppm were assigned to end 2-ethyle-2-oxazoline cationic monomers. Signal of PEG also appeared at 3.6 ppm.

As mentioned above, hydrophobicity or hydrophilicity of star copolymers depend on the terminator reagent. When living POX arms were terminated by diethanolamine, star copolymers were freely soluble in water, whereas termination by *O*-anisidine led to the hydrophobic star copolymers.

Polymerization of ϵ -caprolactone by end functional groups of star copolymers led to the amphiphilic linear-dendritic copolymers (PEG-POX-PCL) (Scheme 1).

Structure of functionalized PEG, PEG-POX star copolymers, and PEG-POX-PCL linear-dendritic

copolymers was evaluated using spectroscopy methods.

Figure 2(a–c) shows the IR spectra of PEG-Cl₄, PEG-POX-OH, and PEG-POX-PCL, respectively. In Figure 2(a), the absorbance band at 1669 cm⁻¹, which is related to the C=N bonds of cyanuric chloride segments, shows that the cyanuric chloride segments are conjugated to the PEG, and PEG is functionalized successfully. In the IR spectra of PEG-POX-OH, the absorbance band at 3300–3000 is related to the hydroxyl end functional groups and the absorbance band at 1660 cm⁻¹ is related to the carbonyl group of POX arms. The IR spectra of PEG-POX-PCL show the absorbance bands of end hydroxyl functional groups of PCL arms, carbonyl groups of POX, and PCL arms at 3300–3100, 1730, and 1660 cm⁻¹, respectively.

Figure 3 shows the ¹H-NMR spectra of PEG-POX-OH linear-dendritic copolymer. This spectra contain the same signals for linear-dendritic copolymers

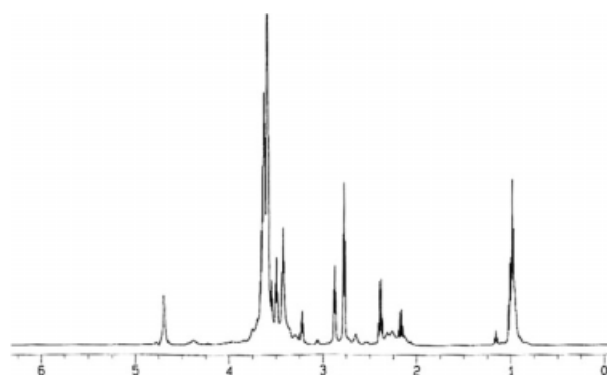


Figure 3 ¹H-NMR spectra of PEG-POX-OH linear-dendritic copolymer.

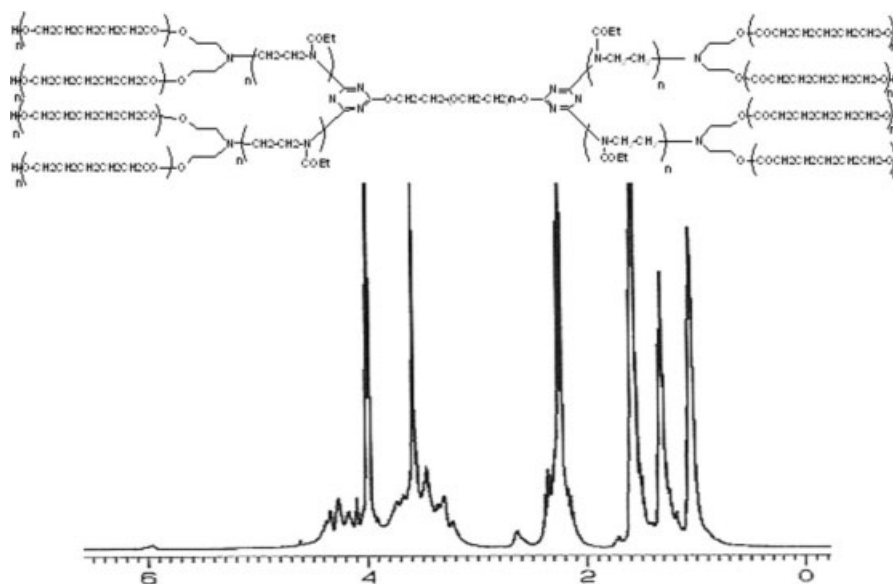


Figure 4 $^1\text{H-NMR}$ spectra of PEG-POX-PCL.

containing living POX arms (Fig. 1), but here the signals of end cationic monomers have disappeared and instead its signals of diethanolamine parts can be seen at 2.9 and 3.5 ppm for $-\text{NCH}_2-$ and $-\text{CH}_2\text{OH}$, respectively.

Figure 4 shows the $^1\text{H-NMR}$ of PEG-POX-PCL in which signals of POX appear at 3.5, 2.2, and 1 ppm for protons of $-\text{CH}_2-\text{N}-$, $-\text{CO}-\text{CH}_2$, and methyl groups, respectively. In this spectra, signals at 4.7–4 and 2.4–2.2 ppm are assigned to the $-\text{CH}_2-\text{O}-$ and $-\text{CO}-\text{CH}_2-$ groups of PCL chains. Signals at 1.3–

1.6 ppm are also related to the other methylene groups of PCL chains. The signal of PEG appears at 3.6 ppm.

Figure 5 shows $^{13}\text{CNMR}$ spectra of PEG-POX-PCL. In this spectra, signals of PCL blocks appeared at 172.6, 63 (h), 33 (d), 27 (g), 24 (e), and 23.5 (f) for the carbonyl group and $[-\text{OCO}-\text{CHd}_2-\text{CHe}_2-\text{CHf}_2-\text{CHg}_2-\text{CHh}_2-\text{O}-]$ building blocks, respectively. Signals of PEG block appeared at 69 and 62 ppm for the $-\text{O}-\text{CH}_2-$ triazine and PEG, respectively. Signals of POX blocks also appeared at 175,

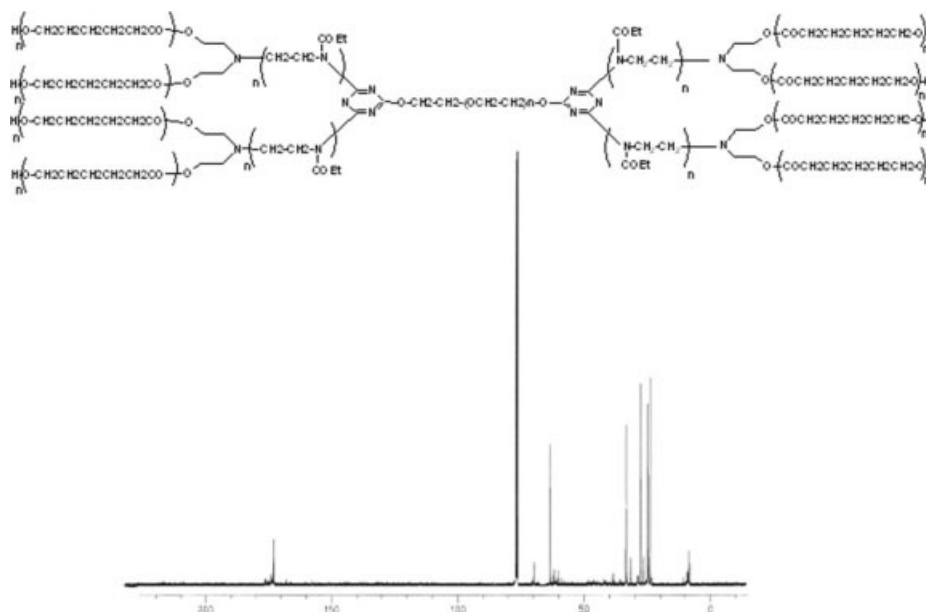


Figure 5 $^{13}\text{C-NMR}$ spectra of PEG-POX-PCL.

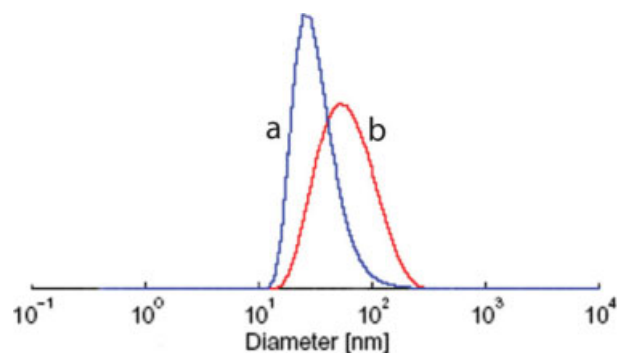


Figure 6 DLS diagram of (a) PEG-POX and (b) PEG-POX-PCL in chloroform solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

26.2, and 8.4–8.7 and 175.42 for the carbonyl group, $-\text{CO}-\text{CH}_2-$, $-\text{CH}_2-\text{N}(\text{CH}_2)_2-$, and methyl groups, respectively.

Size and solution behavior of linear-dendritic macromolecules were investigated using DLS experiments. Figure 6 shows the DLS diagrams of PEG-POX and PEG-POX-PCL in chloroform solvent. The results of DLS experiments show that the diameter of PEG-POX-PCL particles is higher than that for PEG-POX, and the PDI of PEG-POX is narrower than that for PEG-POX-PCL. It seems that all copolymers in chloroform solution are in their aggregation forms, but the bigger size and higher PDI index of amphiphilic linear-dendritic copolymers show that their aggregation behavior probably is different from that for PEG-POX copolymers.

Molecular weights of copolymers were measured using $^1\text{H-NMR}$ and GPC experiments (Table I). The higher calculated molar mass using $^1\text{H-NMR}$ data is expected because copolymers are dendritic macromolecules and their hydrodynamic volume is different with linear polymers used as standard for GPC column. Here the recorded molecular weights by GPC have been used to show the growth of the molecular weight through the different steps of polymerization. The PDI of copolymers measured by DLS is higher than that by GPC. This result shows that particles in the chloroform solution are probably in the micellar form.

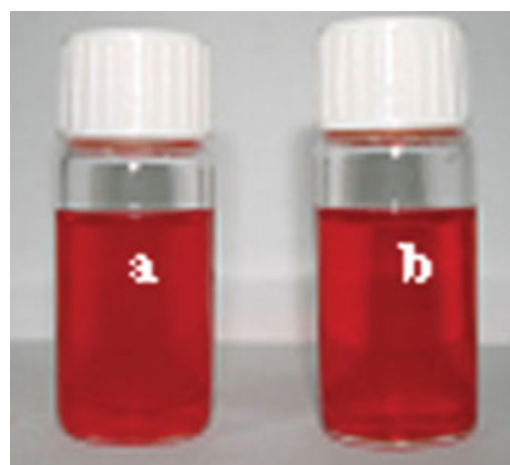


Figure 7 Image of chloroform solution of encapsulated Congo red by (a) PEG-POX and (b) PEG-POX-PCL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Due to their aggregation and micellar behaviors in the solution, linear-dendritic copolymers are promising materials to load the small guest molecules. In this work, Congo red was chosen as a guest molecule for host-guest experiments because it is a polar hydrophilic molecule containing hetero atoms, it is not soluble in the chloroform solution, and loading of this guest molecule can be followed visually.

For loading experiments, linear-dendritic copolymers were dissolved in chloroform solvent and stirred for 1 h; Congo red was then added to this solution, and it was stirred for 2 h. The mixture was filtered and decanted, and clear solution was used for UV experiments.

Figure 7(a,b) shows the image of loaded Congo red in the chloroform solution by PEG-POX containing *O*-anisidine end segments and PEG-POX-PCL, respectively. Chloroform solution of linear-dendritic copolymers is colorless and Congo red is not soluble in the chloroform; hence, changing the color of chloroform solution of copolymers in the presence of Congo red can be assigned to the loading of the Congo red by copolymers.

Figure 8(a,b) shows the chloroform solution of loaded Congo red by PEG-POX containing *O*-

TABLE I
Characteristics of Copolymers Obtained from NMR, DLS, and GPC Data

Sample	$M_{n\text{NMR}}$	$M_{n\text{GPC}}$	PDI_{GPC}	PDI_{DLS}	Diameter (nm)
PEG-POX _a	5000	4200	1.5	1.7	17
PEG-POX _b	8400	6700	1.4	1.8	25
PEG-POX _c	21,000	19,400	1.2	1.4	35
PEG-POX-PCL _a	–	10,100	1.8	2.2	53
PEG-POX-PCL _b	–	18,200	1.4	1.5	72
PEG-POX-PCL _c	–	54,200	1.3	1.4	92

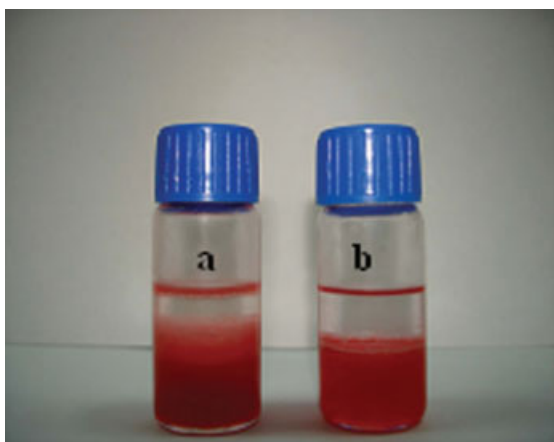


Figure 8 Image of chloroform solution of encapsulated Congo red by (a) PEG-POX-PCL and (b) PEG-POX containing end *O*-anisidine segments in the presence of water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

anisidine end segments and PEG-POX-PCL copolymers in the presence of water after 3 h. It can be seen that the loaded Congo red is not released to the water phase after several hours (Congo red is freely soluble in water). This observation shows that Congo red is trapped by copolymers and is not mixed with copolymers physically. According to these experiments, these linear-dendritic copolymers are promising materials for encapsulation of guest molecules and their long-term release. On the other hand, the interphase of water and chloroform in these two figures is different, which is related to the structure of copolymers. PEG-POX copolymer contains two blocks in which their solution behavior is similar. Its interphase is clear and completely separated, whereas PEG-POX-PCL copolymer contains PEG-POX as the hydrophilic block and PCL as the hydrophobic block in which PEG-POX block is directed toward water and PCL toward organic

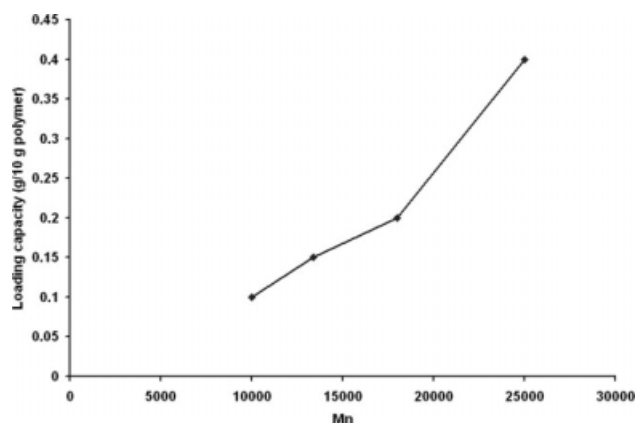


Figure 9 Relation between the molar mass and loading capacity of PEG-POX-PCL in chloroform.

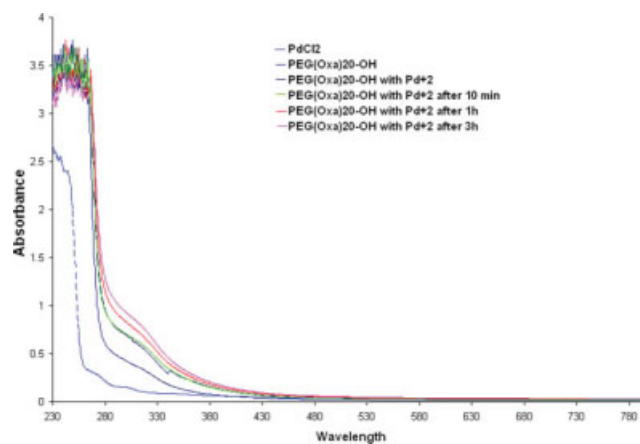


Figure 10 UV spectra of complexation between PdCl₂ and PEG-POX-OH linear-dendritic copolymer in interval times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

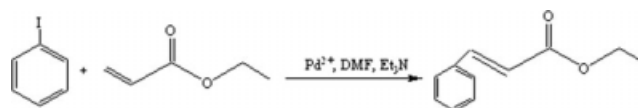
phase; hence its interphase is miscible and is not clear.

The effects of the length of arms on the loading capacity of copolymers was investigated using HPLC and UV-vis. There was good agreement between the results from both procedures. Both experiments showed that the loading capacity of PEG-POX-PCL was higher than that for PEG-POX.

Figure 9 shows the relation between the loading capacities of PEG-POX-PCL copolymers containing PCL arms with different lengths. In this figure, the loading capacity of copolymers increased with increased molecular weight or length of PCL arms. This shows that higher lengths of hydrophobic blocks cause better aggregation in the solvent, which leads to a higher loading capacity.

Linear-dendritic copolymers were able to load inorganic guest molecules. Figure 10 shows the UV spectra of complexation of PdCl₂ by PEG-POX-OH linear-dendritic copolymer. In this figure, the intensity of the metal-ligand charge transfer absorbance band at 290–380 nm increases during the complexation process. In time, the intensity of the metal-ligand charge transfer absorbance band does not increase, showing the highest loading capacity of copolymer.

Loaded palladium ions by linear-dendritic copolymers were used as the nanocatalyst for the Heck reaction between iodobenzene and ethyl acrylate (Scheme 2). Figure 11 shows the GC-Mass results in



Scheme 2 Heck reaction between iodobenzene and ethyl acrylate in the presence of catalyst.

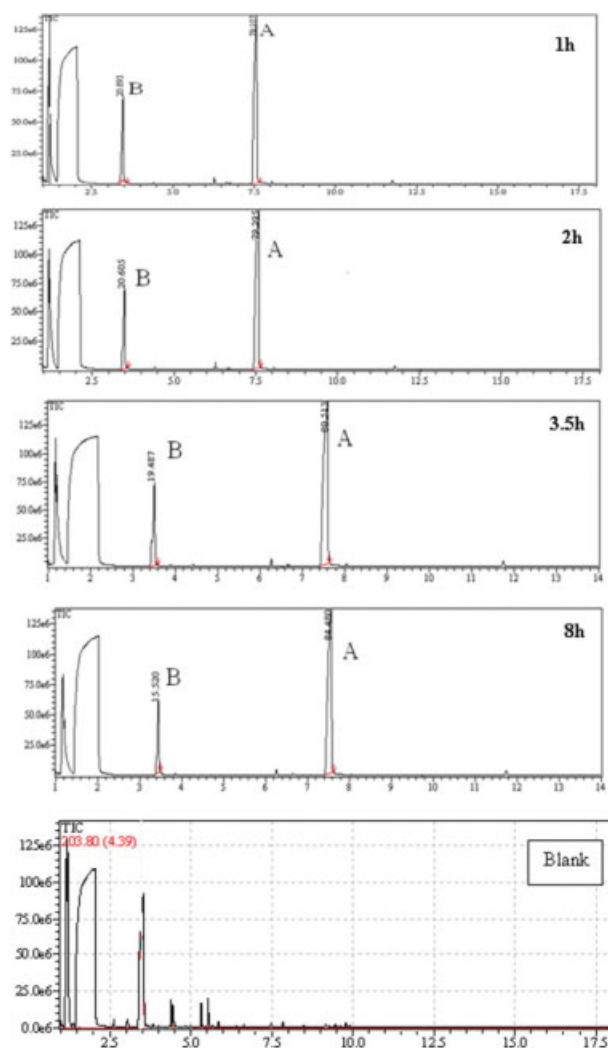


Figure 11 GC mass of mixture of the Heck reaction in the presence of nanocatalyst in interval times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

interval times during the reaction. In this figure, signals A and B are related to the product of Heck reaction and iodobenzene, respectively. The yield of reaction after 1 and 8 h are about 79 and 84%, respectively. The majority of reaction occurred in the first hour, and the rate of reaction in the presence of nanocatalyst was very high. The GC diagram of blank reaction (without catalyst after 24 h) does not show any signal related to the products. These results show that the rate of the Heck reaction is very high in the presence of catalyst and that the linear-dendritic copolymers can be used to transport and support catalysts.

CONCLUSION

Cyanuric chloride and its derivatives are able to initiate the polymerization of oxazoline monomers. Due to its multifunctionality, cyanuric chloride could

be used as initiator for synthesis of star and dendritic macromolecules containing POX arms. The synthesized dendritic macromolecules are able to load small guest molecules. The stability of host-guest systems in the presence of water is high and the rate of release of guest molecules is low. Linear-dendritic copolymers containing PdCl₂ can be used as the nanocatalyst for Heck chemical reactions.

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