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(54) **Title:** MULTI-BLOCK COPOLYMER AND POLYMER ELECTROLYTE

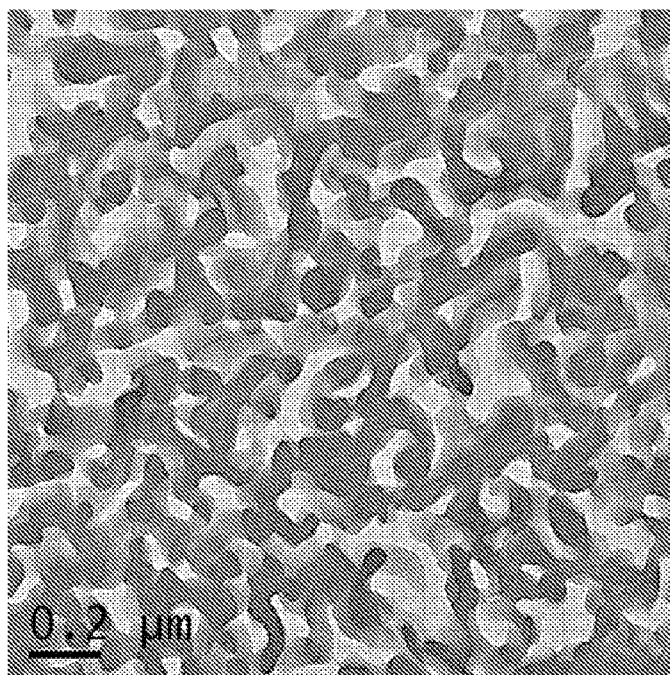


Figure 1

(57) **Abstract:** The present invention provides a multi-block copolymer with polyoxyethylene unit in side chain and a polymer electrolyte containing the multi-block copolymer. Since the multi-block copolymer has a number of block of larger than 3, it can completely avoid crystallization and is easier to has phase separation morphology, especially co-continuous phase morphology, and thus has better performance. For the polymer electrolyte, co-continuous phase morphology can be achieved in a wide range of segment A content. The polymer electrolyte of the present invention is thus greatly improved in ionic conductivity and mechanical properties.



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MULTI-BLOCK COPOLYMER AND POLYMER ELECTROLYTE

TECHNICAL FIELD

The present invention relates to a multi-block copolymer and a polymer electrolyte material used for lithium ion secondary battery.

BACKGROUND ART

Lithium ion secondary battery is a promising green chemical power source with higher energy density, higher output voltage, and shorter charging time than other secondary batteries, and thus it has great economic and social benefit. For electrolyte of lithium ion secondary battery, liquid electrolyte has traditionally been used. However, the liquid electrolyte is prone to leakage, which may cause safety problems and spoil long-term reliability.

At present, the most promising solution is application of solid electrolyte materials such as inorganic electrolyte or polymer electrolyte (solid) instead of liquid electrolytes. The inorganic solid electrolyte potentially has the highest lithium ion conductivity among solid electrolyte materials. However, it has drawbacks of low processability and high interfacial resistance to electrode. Accordingly, thanks to advantages in weight, flexibility and processability, research and development of solid polymer electrolyte have been actively pursued.

As a solid polymer electrolyte material, it is common to use polyethylene oxide (or polyoxyethylene, abbreviated as PEO) which are capable of forming a complex with electrolyte salts such as lithium salts, possessing lithium ion conductivity. However, it has so high crystallinity that the movement of PEO chains is extremely restricted, resulting in low lithium ion conductivity.

In order to reduce the crystallinity of polymer electrolyte containing PEO unit and improve the lithium ion conductivity, two directions of researches have been conducted. One is introducing PEO units into main chains of polymer, and the other is into side chains. For researches on polymer electrolyte containing PEO unit in the main chains, PEO-b-polystyrene (abbreviated as PS) di-block copolymer with certain content of PEO showed lamellar phase separation morphology (*Macromolecules*, 2007(40), 4578 ~ 4585). Additionally, PS-b-PEO-b-PS tri-block copolymer which showed various phase

separation morphologies, mechanical and electrochemical properties were reported (CN 200780020101.3). However, those di-block and tri-block copolymers still showed lower lithium ion conductivity than $1 \times 10^{-5} \text{S/cm}$ at ambient temperature which may possibly due to the limited mobility of PEO unit in the main chain and resulting in low lithium ion conductivity.

In order to improve the mobility of PEO unit and realize higher lithium ion conductivity, polymer electrolyte with PEO unit in side chains has been studied. For example, the lithium ion conductivity of a polymer electrolyte comprising a copolymer of ABA type (methoxy polyethyleneglycol methacrylate (A) containing polyoxyethylene ion conducting unit as a block for ion conduction and styrene (B) as a block for mechanical property of electrolyte which does not contain ion conducting unit) (*Makromol. Chem.*, 1989 (190) 1069 ~ 1078) or BAB type (CN0381732.3 and *Journal of Power Sources*, 2005 (146) 386 ~ 390) was improved by 1~2 order of magnitudes over those comprising a polymer with PEO units in its main chains, reaching $1 \times 10^{-4} \text{S/cm}$. To further improve lithium ion conductivity and mechanical property of the electrolyte, control of phase separation morphology is essential. As reported in Patent (CN0381732.3), co-continuous phase separation morphology is suitable for compatibility between ion conductivity and mechanical property of electrolyte. However, as reported in *Journal of Power Sources*, 2005 (146), 386 ~ 390, co-continuous phase morphology can only be achieved for tri-block polymers with higher content of segment A than 70% and lower content of segment B which may result in low mechanical properties of polymer electrolyte membrane.

As described above, polymer electrolyte materials of prior art were insufficient to support lithium ion conductivity and mechanical property of electrolyte membranes at same time, failing to achieve long-term durability and industrially useful material for lithium ion battery.

DISCLOSURE OF INVENTION

In view of the state of the art described above, it is an object of present invention to provide polymer electrolyte material which has both high lithium ion conductivity and excellent mechanical properties, which achieves to form a polymer solid electrolyte battery with high energy density, high output voltage, short charging times, and high

reliability.

The present invention employs following means so as to meet such an object. Namely, the polymer of the present invention is a multi-block copolymer with PEO repeating unit in side chains and shows co-continuous phase separation morphology in all range of segment content.

According to the present invention, it is possible to provide a polymer electrolyte material which has high lithium ion conductivity and excellent mechanical strength at same time, which also can form a polymer solid electrolyte battery with high energy density, high output voltage, short charging times, and high reliability.

Hereinafter, the present invention will be described in detail.

The present invention is featured as follows;

A multi-block copolymer possesses the structure of formula (P1):

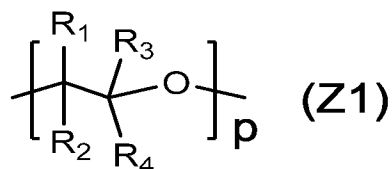


wherein segment A has polyoxyethylene repeating unit in the side chain thereof; segment B has no polyoxyethylene repeating unit; n is a positive integer; and when $n \geq 2$, a and b are independently 0 or 1, and when $n=1$, $a=b=1$.

In formula (P1), larger n is better for obtaining co-continuous phase separation morphology. Co-continuous phase separation morphology is one kind of morphological structures for phase separation. The type of morphology basically depends on the content of segment A or B in the copolymer. For example, the kind of phase separation morphology, such as sphere, cylinder, lamellar, varies depending on the segment content of A or B, as reported in *Macromolecules*, 2007, 40, 4578-4585; *Annual Review of Physical Chemistry*, 41, 1990, 525. And commonly, co-continuous phase separation morphology can only be achieved in a narrow range of segment content and is always dependent of segment content. However, the inventors have overcome the difficulty by making the multi-block copolymer with more than 4 alternately recurring segments as shown in formula (P1).

In formula (P1), segment means a partial structure of multi-block polymer with formula weight of more than 2000 and combining one or more kinds of repeating units.

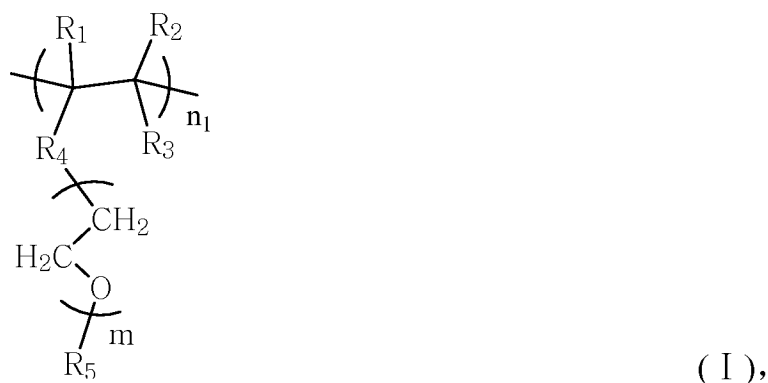
PEO repeating unit in formula (P1) is described in formula (Z1):



wherein $\text{R}_1\text{-R}_4$ are independently H or C1-C10 alkyl; p is a positive integer.

In formula (Z1), $\text{R}_1\text{-R}_4$ are preferably H or C1-C5 alkyl in terms of manufacturing cost, more preferably H or C1-C3 alkyl in terms of lithium ion conductivity. p is preferably a positive integer of 2-50 in terms of crystallinity and manufacturing cost, more preferably 5-30 in terms of ion conductivity.

More preferable structure for segment A is as follows:

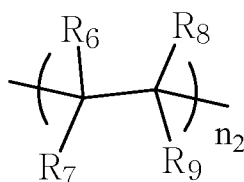


wherein $\text{R}_1\text{-R}_3$ are independently H or C1-C10 alkyl, R_4 is $\text{---} \text{C}(=\text{O}) \text{---} \text{O} \text{---}$ or $\text{---} \text{C}(\text{H}_2) \text{---} \text{C}_6\text{H}_4 \text{---}$, R_5 is H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-hexyl, or phenyl, m is an integer of 2 to 50, and n_1 is an integer of 10 to 500.

In formula (I), $\text{R}_1\text{-R}_3$ are preferably H or C1-C5 alkyl in terms of manufacturing cost, more preferably H, methyl, ethyl in terms of lithium ion conductivity. R_5 is preferably H, methyl, or ethyl for cost and ion conductivity reasons. m is preferably a positive integer of 5 to 30 and n_1 is preferably a positive integer of 20 to 300 in terms of manufacturing cost.

Because the copolymer has more than 4 alternately recurring segments (ABAB, BABA), and the PEO unit is located in its side chain, the crystallinity of the copolymer is reduced and higher lithium ion conductivity is achieved consequently.

In formula (P1), the structure of segment B which has no polyoxyethylene repeating unit can be shown by formula (II):



(II),

wherein $R_6 \sim R_8$ are independently H or C1~C10 alkyl, R_9 is phenyl, p-methylphenyl, m-methyl styrene, p-fluorophenyl, nitrile or carbomethoxy, n_2 is a positive integer of 10 to 500.

In formula (II), $R_6 \sim R_8$ are preferably H, methyl, or ethyl for manufacturing and cost advantages. R_9 is preferably phenyl, p-methylphenyl or carbomethoxy for cost advantages. n_2 is preferably 20 to 300 in terms of compatibility of ion conductivity and mechanical property.

The multi-block copolymer in the present invention can be prepared by living radical polymerization method, preferably Atom Transfer Radical Polymerization method (ATRP). Block number and reaction steps can be adjusted by halogen atoms of organic halogen initiator.

Transition metal complex (transition metal halide / ligand complexes) can be used as a catalyst. For transition metal halide, it may be halide of copper, ruthenium, iron, rhenium, nickel or palladium. In particular, it is preferably selected from the group consisting of copper bromide, copper chloride, dichlorotris(triphenylphosphine) ruthenium, dichlorotris(tributylphosphine) ruthenium, ferrous chloride and ferrous bromide. For ligand, it may be amines or phosphines. In particular, it is preferably selected from the group consisting of 4,4'-bipyridine (bpy), pentamethyldiethylenetriamine (PMDETA), trimethylsilyl-diethylamine (Me_6TREN), 4,4'-bis(nonyl)-2,2'-bipyridine (dNbpy) and tris(2-pyridylmethyl)amine (TPMA).

Initiator used for the living radical polymerization may be organohalogen compound comprising one or two halogen atoms. In particular, it is preferably selected from the group consisting of dichloromethane, 1,2-dichloroethane, chlorobenzene, dichlorobenzene, 2,2-dichloroacetophenone, ethyl 2-bromopropionate, diphenylmethane, bromodiphenylmethane and tosyl chloride. Additionally, the number of halogen atoms will have an effect on the polymerization process and the number of blocks. Specifically, when organohalogen compound with one halogen atom is used, the reaction process should have $(a+b+2n)$ steps to obtain the multi-block copolymer of formula (P1). When

organohalogen compound with two halogen atoms is used, only n steps are required to obtain the same polymer. The number of halogen atoms mentioned here refers to the number of halogen atoms which can be effectively induced, and does not include the ones without activity, for example, the halogen atom of acyl chloride can not be counted because of no activity for initiating reaction.

Relative to conventional synthesis for A-B-A or B-A-B tri-block copolymers, polymerization conditions used to prepare multi-block copolymers with block number greater than 3 should be more rigorous and complex. Such multi-block copolymers can not be obtained constantly by the conventional reaction conditions, because the growth of new segment becomes more difficult as the molecular weight increases. In order to prepare multi-block copolymer with block number greater than 3, special process or method should be introduced, for example, gradient temperature is used to obtain a homogeneous reaction system or bulk polymerization to increase activity. For example, to synthesize quadri-block copolymer of A-B-A-B type, tri-block copolymer of A-B-A type with one halogen atom is used as a macromolecular initiator and, because of high M_n solubility, is not so good. If synthesis is carried out in a common way by directly heating, most of the macromolecular initiator is insoluble, and an asymmetrical reaction system is thus formed. Therefore, the system is firstly heated to low temperature in low rate, such as 50°C and 3°C/min, to completely dissolve the macromolecular initiator. Then, the system is further heated to final reaction temperature still in low rate and polymerization is conducted. Any method which is effective to increase uniformity for system or reactivity can be used to prepare the multi-block copolymer provided in the present invention.

Another object of the present invention is to provide a polymer electrolyte, comprising a multi-block copolymer described above and an electrolyte salt. In case that the number of blocks is greater than 3, co-continuous phase morphology can be achieved in a wide range of segment A content. This will lead to easy adjustment of ionic conductivity and mechanical properties of polymer electrolyte, and the overall performance of the polymer electrolyte can thus be greatly improved.

There are no particular restrictions on the electrolyte salt used in the present invention. Suitable examples include alkali metal salts, quaternary ammonium salts or transition metal salts. For electrolytes that display a large dissociation constant within

polymer electrolyte, lithium salts are preferred. For cost and performance advantages, lithium salts selected from the group consisting of lithium bis(trifluoromethane sulfonimide) (LiTFSI), lithium perchlorate (LiClO_4), lithium tri-fluoromethanesulfonate (LiCF_3SO_3), lithium hexa-fluorophosphate (LiPF_6), lithium tetra-fluoroborate (LiBF_4) and mixtures thereof are preferably used.

The amount of electrolyte salt added is typically within a range from 0.005 to 80 mol%, relative to the molar quantity of polyoxyethylene units in the copolymer. Considering balance of ionic conductivity and mechanical properties, the amount of the electrolyte salt is preferably 0.01 to 20 mol%. The method of adding electrolyte salt to the copolymer is not restricted. Solution in tetrahydrofuran, chloroform, N-methyl pyrrolidone or toluene is preferably used, but mechanical mixing at room temperature or under heat can also be applied.

Different from conventional polymer electrolyte, micro phase separation morphology, especially co-continuous phase morphology can be achieved in a wide range of segment A content. At same time, the content of segment A of 50~99% which is preferable in terms of high lithium ion conductivity can be achieved with co-continuous phase morphology. Micro phase separation morphology, especially co-continuous phase morphology helps to keep the transport (ion conductive) properties of segment A and support (mechanical) properties of segment B at same time.

Molding the aforementioned solid polymer electrolyte into sheet, membrane, or film form is particularly desirable in terms of processability. The sheet-like solid polymer electrolyte can be produced by any coating techniques, such as roll coating, curtain coating, spin coating, dipping, or casting. Using one of these techniques, film of polymer solid electrolyte is formed on the surface of a substrate, and the substrate is subsequently removed to yield the solid polymer electrolyte sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a transmission electron microscope photograph showing a cross-section of the electrolyte film in Example 1. Co-continuous phase morphology can be observed.

Figure 2 is a transmission electron microscope photograph showing a cross-section of the electrolyte film in Example 2. Co-continuous phase morphology can be observed.

Figure 3 is a transmission electron microscope photograph showing a cross-section

of the multi-block copolymer in Comparative Example 1. For multi-block copolymer with polyoxyethylene unit in main chain, lamellar phase morphology can be observed.

Figure 4 is a transmission electron microscope photograph showing a cross-section of the electrolyte film in Comparative Example 3. When the content of segment A is 11.8 wt%, “sea-island” phase morphology can be observed.

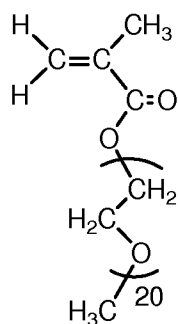
DESCRIPTION OF THE PREFERRED EMBODIMENTS

More detailed description of the present invention is shown as follows using a series of examples, but the present invention is not limited thereto.

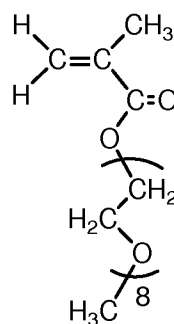
Raw materials used:

1. Monomer corresponding to segment A:

(a) Poly(ethylene glycol) methyl ether methacrylate

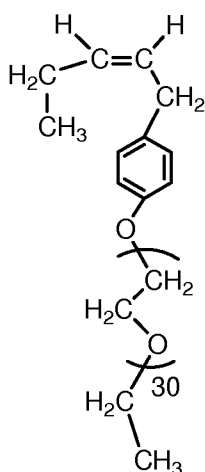


PEGMA-1 (m=20, $M_n=980$)



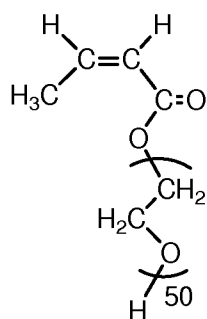
PEGMA-2 (m=8, $M_n=450$) ,

(b) Poly(ethylene glycol) ethyl ether allylbenzene



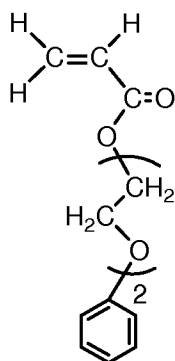
(m=30, $M_n=1520$) ,

(c) Poly(ethylene glycol) methacrylate



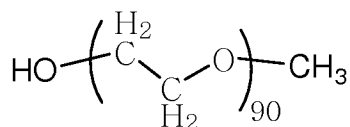
($m=50$, $M_n=2300$),

(d) Poly(ethylene glycol) phenoxy acrylate



($m=2$, $M_n=240$),

(e) Poly(ethylene glycol) methyl ether

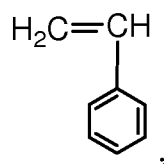


($M_n=4000$).

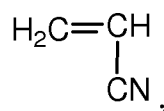
All monomers were purchased from Sigma-Aldrich Co.Ltd.

2. Monomer corresponding to segment B:

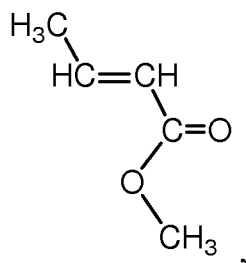
(a) Styrene (St)



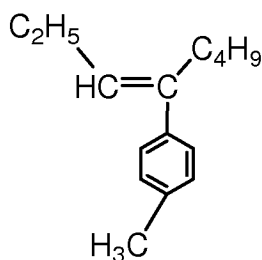
(b) Acrylonitrile (AN)



(c) Methyl acrylate



(d) 4- methyl phenyl-3- octylene



All monomers were purchased from Sigma-Aldrich Co. Ltd.

3. Initiator

Dichlorobenzene, 2,2-dichloroacetophenone, ethyl 2-bromopropionate: purchased from Sigma-Aldrich Co. Ltd.

Dichloromethane: purchased from Sinopharm Chemical Reagent Co. Ltd. and purified by refluxing with Na to remove water before using.

4. Transition metal halide

CuBr, CuCl: purchased from Sinopharm Chemical Reagent Co. Ltd. and purified with acetic acid and methanol before using.

Dichlorotris (triphenylphosphine) ruthenium, ferrous bromide: purchased from Sigma-Aldrich Co. Ltd. and used without further purification.

5. Ligand

4,4'-bipyridine (bpy), pentamethyldiethylenetriamine (PMDETA), trimethylsilyl-diethylamin (Me₆TREN): purchased from Sigma-Aldrich Co. Ltd. and used without further purification.

6. Lithium salt

Lithium bis(trifluoromethane sulfonimide) (LiTFSI), lithium perchlorate (LiClO₄), lithium tri-fluoromethanesulfonate (LiCF₃SO₃), lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄): purchased from Sigma-Aldrich Co. Ltd. and used without further purification.

7. Other reagents

Toluene: purchased from Sinopharm Chemical Reagent Co. Ltd. and purified by refluxing with Na to remove water before using.

Tetrahydrofuran (THF), diethyl ether anhydrous, n-hexane, aluminum oxide, N-methyl pyrrolidone (NMP), deuteriochloroform, aluminium isopropoxide, ethylene oxide, 120# gasoline: purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification.

Measurement conditions for various properties used:

- A. Number average molecular weight of polymer: Gel Permeation Chromatography (GPC) (LC-20, Japan), tetrahydrofuran as solvent and mobile phase.
- B. Content of segment A in polymer (wt%): ^1H NMR (JEOL ECX-400P, Japan), deuteriochloroform as solvent.
- C. Phase morphology: Transmission Electron Microscope (TEM) (JEM2010, Japan), sampling by ice-embedding and slicing at -80°C .
- D. Crystallinity: Differential Scanning Calorimeter (DSC) (Q100, American), N_2 protection, $-80^\circ\text{C}\sim 200^\circ\text{C}$, $20^\circ\text{C}/\text{min}$.
- E. Mechanical properties: Dynamic Mechanical Analyzer (DMA) (TA DMA Q800, American), stretching mode, 1Hz, room temperature $\sim 400^\circ\text{C}$, $3^\circ\text{C}/\text{min}$.
- F. Lithium ion conductivity: Electrochemical workstation (VSP Japan), polymer electrolyte membrane is put into the test unit (HS Test Cell, Japan Hohsen) in glove box and then tested after being kept more than 1 hour at ambient temperature (23°C).

Example 1 (Preparation of quadri-block copolymer of A-B-A-B type and corresponding polymer electrolyte, in which poly(poly(ethylene glycol) methyl ether methacrylate) (denoted as P(PEGMA)) was used as segment A and polystyrene (denoted as PS) was used as segment B)

(1) Synthesis of segment A

To 15 ml of toluene, 15.5 g of poly(ethylene glycol) methyl ether methacrylate (PEGMA-1, $M_n=980$, $m=20$, 15.8 mmol) was added and dissolved under N_2 atmosphere. Then, 45.3 mg (0.316 mmol) of CuBr and 98.65 mg (0.732 mmol) of bpy were added into the solution. After 10 min of stirring, 57.2 mg (0.316 mmol) of ethyl

2-bromopropionate was added and heated to 90°C. After polymerization for 30 hours, the solution was cooled immediately in ice/water bath to stop the reaction. Then, the solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified P(PEGMA)-1 was obtained. The P(PEGMA)-1 had a M_n of 42000 and a M_w/M_n of 1.12, and the GPC curve thereof showed a single symmetrical peak.

(2) Synthesis of di-block copolymer of A-B type

Under protection of N₂, 8.0 g (0.094 mmol) of P(PEGMA)-1, 9.31 mg (0.094 mmol) of CuCl, 16.33 mg (0.094 mmol) of PMDETA and 10 g (0.096 mmol) of St were blended to form a reaction system. Then the reaction system was sealed and the reaction temperature was raised to 110°C under stirring. Polymerization was carried out for 3 hours. Then reaction system was cooled immediately in ice/water bath to stop the polymerization. Solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted St, and purified white powder of P(PEGMA)-b-PS di-block copolymer (A-B type) was obtained. The di-block copolymer had of a M_n of 80000 and a M_w/M_n of 1.32, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 52.5 wt%.

(3) Synthesis of tri-block copolymer of A-B-A type

Under argon atmosphere, 10.92 mg (0.075 mmol) of CuBr and 23.77 mg (0.15 mmol) of bpy were added to 10 ml of toluene to form a reaction system. After 10 min of stirring, a catalyst/ligand complex was formed. 3.13 g (3.0 mmol) of PEGMA-1($M_n=980$, $m=20$) was added and dissolved with stirring under argon atmosphere for 15 min. Then 1.2 g (0.015 mmol) of macromolecular initiator P(PEGMA)-b-PS was added into the reaction system. Then reaction system was sealed. After the di-block copolymer was dissolved completely, the reaction temperature was increased to 90°C. Polymerization was carried out for 40 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers, and purified white powder of

P(PEGMA)-b-PS-b-P(PEGMA) tri-block copolymer (A-B-A type) was obtained. The tri-block copolymer had a M_n of 125000 and a M_w/M_n of 1.48, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 69.6 wt%.

(4) Synthesis of quadri-block copolymer of A-B-A-B type

Under argon atmosphere, 11.75 g (0.094 mmol) of macromolecular initiator P(PEGMA)-b-PS-b-P(PEGMA), 9.31 mg (0.094 mmol) of CuCl, 16.33 mg (0.094 mmol) of PMDETA and 10g (0.096 mol) of St were added to 10 ml of toluene to form a reaction system. Then the reaction system was sealed and the reaction temperature was raised to 50°C in a rate of 3°C/min. After 30 minutes of agitation to completely dissolve the macromolecular initiator, the reaction temperature was further raised to 110°C in a rate of 3°C/min and polymerization was carried out for 3 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted monomers and the purified white powder of P(PEGMA)-b-PS-b-P(PEGMA)-b-PS quadri-block copolymer (A-B-A-B type) was obtained. The quadri-block copolymer had a M_n of 160000 and a M_w/M_n of 1.39, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 54.4 wt%.

(5) Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of the dried quadri-block copolymer was dissolved in 15 ml of toluene, and 0.35 g of LiTFSI (the amount of added Li salt is 10 mol% relative to polyoxyethylene repeating unit) was added into the solution. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the thus obtained polymer solid electrolyte membrane was 40 μm.

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no

crystallinity.

According to the results of DMA, the initial modulus of the polymer solid electrolyte membrane was 4.2 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity thereof was found to be 8.9×10^{-4} S/cm by measuring at 23°C using an electrochemical workstation.

Example 2 (Preparation of penta-block copolymer of A-B-A-B-A type and corresponding polymer electrolyte, in which P(PEGMA) was used as segment A and PS was used as segment B)

The quadri-block copolymer of P(PEGMA)-b-PS-b-P(PEGMA)-b-PS (A-B-A-B type) prepared in Example 1 was used as a macromolecular initiator to prepare penta-block copolymer.

(1) Synthesis of penta-block copolymer of A-B-A-B-A type

Under argon atmosphere, 10.92 mg (0.075 mmol) of CuBr and 23.77 mg (0.15 mmol) of bpy were added to 5.2 ml of toluene to form a reaction system. After 10 min of stirring, a catalyst/ligand complex was formed. 3.13 g (3.0 mmol) of PEGMA-1 ($M_n=980$, $m=20$) was added and dissolved with stirring for 15 min. Then the reaction system was sealed, and after macromolecular initiator was dissolved completely, the reaction temperature was raised to 90°C. Polymerization was carried out for 100 hours. Then reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified white powder of P(PEGMA)-b-PS-b-P(PEGMA)-b-PS-b-P(PEGMA) penta-block copolymer (A-B-A-B-A type) was obtained. The penta-block copolymer had a M_n of 320000 and a M_w/M_n of 1.41, the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 77.2 wt%.

By repeating Example 1-(4) and Example 2-(1), multi-block copolymer with block number of six, seven, eight or more can be obtained.

(2) Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of the dried penta-block copolymer was dissolved in 10 ml of NMP, and 0.33 g of LiBF_4 (the amount of added Li salt is 20 mol% relative to polyoxyethylene repeating unit) was added into the solution. Then solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C . The thickness of the obtained polymer solid electrolyte membrane was 40 μm .

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no crystallinity.

According to the results of DMA, the initial modulus of the polymer solid electrolyte membrane was 3.7 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be $3.5 \times 10^{-3} \text{ S/cm}$ by measuring at 23°C using electrochemical workstation.

Example 3 (Preparation of penta-block copolymer of A-B-A-B-A type and corresponding polymer electrolyte, in which P(PEGMA) was used as segment A and PS was used as segment B)

(1) Synthesis of segment A

To 25 ml of toluene, 18.0 g of PEGMA-2 ($M_n=450$, $m=8$, 40.0 mmol) was added and dissolved under N_2 atmosphere. Then 57.34 mg (0.40 mmol) of CuBr and 107.82 mg (0.80 mmol) of bpy were added into the solution. After 10 min of stirring, 75.57 mg (0.40 mmol) of 2,2-dichloroacetophenone was added and heated to 90°C . After polymerization for 25 hours, the solution was cooled immediately in ice/water bath to stop the reaction. Then, the solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction

product was washed with diethyl ether anhydrous to remove unreacted monomers and purified P(PEGMA)-2 was obtained. The P(PEGMA)-2 had a M_n of 6000 and a M_w/M_n of 1.14, and the GPC curve thereof showed a single symmetrical peak.

(2) Synthesis of tri-block copolymer of B-A-B type

Under protection of N_2 , 0.43 g (0.071 mmol) of P(PEGMA)-2, 20.28 mg (0.141 mmol) of CuBr, 24.50 mg (0.141 mmol) of PMDETA and 20.56 g (0.197 mmol) of St were blended to form a reaction system. Then the reaction system was sealed, and after 10 min of stirring, the reaction temperature was raised to 110°C. Polymerization was carried out for 5 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted St and purified white powder of PS-b-P(PEGMA)-b-PS tri-block copolymer (B-A-B type) was obtained. The tri-block copolymer had a M_n of 51000 and a M_w/M_n of 1.32, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 11.8 wt%.

(3) Synthesis of penta-block copolymer of A-B-A-B-A type

Under argon atmosphere, 13.10 mg (0.09 mmol) of CuBr and 28.52 mg (0.18 mmol) of bpy were added to 3 ml of toluene to form a reaction system. After 10 min of stirring, a catalyst/ligand complex was formed. 1.62 g (3.6 mmol) of PEGMA-2 ($M_n=450$, $m=20$) was added and dissolved by 15 min of stirring. Then 0.92 g (0.018 mmol) of macromolecular initiator PS-b-P(PEGMA)-b-PS was added into the reaction system. Then the reaction system was sealed, and after the tri-block copolymer was dissolved completely, the reaction temperature was raised to 90°C in a rate of 1.5°C/min. Polymerization was carried out for 100 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified white powder of P(PEGMA)-b-PS-b-P(PEGMA)-b-PS-b-P(PEGMA) penta-block copolymer (A-B-A-B-A type) was obtained. The penta-block copolymer had a M_n of 59000 and a M_w/M_n of 1.37, and the GPC curve thereof showed a single symmetrical peak, and the

content of segment A (f_A) was 23.7 wt%.

(4) Preparation of polymer solid electrolyte membrane and estimation of properties

1g of the dried penta-block copolymer was dissolved in 15ml of NMP, and 0.03g of LiTFSI (the amount of added Li salt is 2mol% relative to polyoxyethylene repeating unit) was added into the solution. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the obtained polymer solid electrolyte membrane was 40μm.

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no crystallinity.

According to the results of DMA, the initial modulus of the polymer solid electrolyte membrane was 3.9 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be 4.5×10^{-4} S/cm by measuring at 23°C using electrochemical workstation.

Example 4 (Preparation of septu-block copolymer of B-A-B-A-B-A-B type and corresponding polymer electrolyte, in which P(PEGMA) was used as A segment and PS was used as B segment)

Penta-block copolymer of P(PEGMA)-b-PS-b-P(PEGMA)-b-PS-b-P(PEGMA) (A-B-A-B-A type) prepared in Example 3 was used as macromolecular initiator to prepare septu-block copolymer.

(1) Synthesis of hepta-block copolymer of B-A-B-A-B-A-B type

Under protection of N₂, 4.40 g (0.071 mmol) of macromolecular initiator (A-B-A-B-A type), 20.28 mg (0.141 mmol) of CuBr, 24.50 mg (0.141 mmol) of PMDETA and 14.69 g (0.141 mmol) of St were blended to form a reaction system was

thus formed. Then the reaction system was sealed and the reaction temperature was raised to 50°C in a rate of 3°C/min under stirring. After 20 min of stirring to completely dissolve the macromolecular initiator, the reaction temperature was further raised to 110°C in a rate of 3°C/min. Polymerization was carried out for 12 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted St and purified white powder of PS-b-P(PEGMA)-b-PS-b-P(PEGMA)-b-PS-b-P(PEGMA)-b-PS as hepta-block copolymer (B-A-B-A-B-A-B type) was obtained. The hepta-block copolymer had a M_n of 128000 and a M_w/M_n of 1.26, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 10.9 wt%.

By repeat of Example 3-(3) and Example 4-(1), multi-block copolymer with block number of nine, eleven, thirteen or more can be obtained.

(2) Preparation of polymer solid electrolyte membrane and estimation of properties

10 g of the dried hepta-block copolymer was dissolved in 100 ml of NMP, and 0.26 mg of LiClO₄ (the amount of added Li salt is 0.01 mol% relative to polyoxyethylene repeating unit) was added into the solution. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the obtained polymer solid electrolyte membrane was 50 μm.

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no crystallinity.

According to the results of DMA, the initial modulus of the polymer solid electrolyte membrane was 4.7 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be 9.6×10^{-4} S/cm at by measuring at 23°C using

electrochemical workstation.

Example 5 (Preparation of penta-block copolymer of A-B-A-B-A type and corresponding polymer electrolyte, in which poly(poly(ethylene glycol) ethylic ether allylbenzene) was used as segment A and poly(acrylonitrile) (denoted as PAN) was used as segment B)

(1) Synthesis of A segment

To 50 ml of toluene, 60.8 g of poly(ethylene glycol) ethylic ether allylbenzene ($M_n=1520$, $m=30$, 40.0 mmol) was added and dissolved under N_2 atmosphere. Then 57.34 mg (0.40 mmol) of CuBr and 107.82 mg (0.80 mmol) of bpy were added into the solution. After 10 min of stirring, 33.97 mg (0.40 mmol) of dichloromethane was added and heated to 90°C. After polymerization for 45 hours, the solution was cooled immediately in ice/water bath to stop polymerization. Then, the solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed by diethyletheranhydrous to remove unreacted monomer and purified poly(poly(ethylene glycol) ethylic ether allylbenzene) was obtained. $M_n=54000$, $M_w/M_n=1.21$, curve of GPC showed single symmetrical peak.

(2) Synthesis of tri-block copolymer of B-A-B type

Under protection of N_2 , 3.83 g (0.071 mmol) of poly(poly(ethylene glycol) ethylic ether allylbenzene), 20.28 mg (0.141 mmol) of CuBr, 24.50 mg (0.141 mmol) of PMDETA and 10.44 g (0.197 mmol) of AN were blended to form a reaction system. Then the reaction system was sealed, and after 10 min of stirring, the reaction temperature was increased to 110°C. Polymerization was carried out for 10 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted monomers and purified white powder of tri-block copolymer (B-A-B type) was obtained. The tri-block copolymer had a M_n of 73000 and a M_w/M_n of 1.35, and the GPC curve thereof showed a single symmetrical peak.

(3) Synthesis of penta-block copolymer of A-B-A-B-A type

Under argon atmosphere, 13.10 mg (0.09 mmol) of CuBr and 28.52 mg (0.18 mmol) of bpy were added to 5 ml of toluene to form a reaction system. After 10 min of stirring, a catalyst/ligand complex was formed. 5.47 g (3.6 mmol) of poly(ethylene glycol) ethylic ether allylbenzene ($M_n=1520$, $m=30$) was added and dissolved with stirring for 15 min. Then 1.31 g (0.018 mmol) of macromolecular initiator of tri-block copolymer prepared in Example 5-(2) was added into the reaction system. Then the reaction system was sealed, and after the tri-block copolymer was dissolved completely, the reaction temperature was raised to 90°C in a rate of 1.5°C/min. Polymerization was carried out for 100 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the product was washed with diethyl ether anhydrous to remove unreacted monomers and purified white powder of poly(poly(ethylene glycol) ethylic ether allylbenzene)-b-PAN-b-poly(poly(ethylene glycol) ethylic ether allylbenzene)-b-PAN-b-poly(poly(ethylene glycol) ethylic ether allylbenzene) penta-block copolymer (A-B-A-B-A type) was obtained. The penta-block copolymer had a M_n of 96000 and a M_w/M_n of 1.56, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 80.2 wt%.

(4) Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of the dried penta-block copolymer was dissolved in 12 ml of NMP, and 0.14 mg of $LiPF_6$ (the amount of added Li salt is 0.005 mol% relative to polyoxyethylene repeating unit) was added into the solution. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the obtained polymer solid electrolyte membrane was 50 μm .

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no crystallinity.

According to the results of DMA, the initial modulus of the polymer solid

electrolyte membrane was 2.8 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be 6.2×10^{-4} S/cm by measuring at 23 °C using electrochemical workstation.

Example 6 (Preparation of penta-block copolymer of A-B-A-B-A type and corresponding polymer electrolyte, in which poly(poly(ethylene glycol) methacrylate) was used as segment A and poly(methyl acrylate) was used as segment B)

(1) Synthesis of segment A

To 100 ml of toluene, 92.0 g of poly(ethylene glycol) methacrylate ($M_n=2300$, $m=50$, 40.0 mmol) was added and dissolved under N_2 atmosphere. Then 383.53 mg (0.40 mmol) of dichlorotris(triphenylphosphine) ruthenium and 184.32 mg (0.80 mmol) of Me_6TREN were added into the solution. After 10 min of stirring, 75.57 mg (0.40 mmol) of 2,2-dichloroacetophenone was added and heated to 90 °C. After polymerization for 45 hours, the solution was cooled immediately in ice/water bath to stop the polymerization. Then, the solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified poly(poly(ethylene glycol) methacrylate) was obtained. The poly(poly(ethylene glycol) methacrylate) had a M_n of 75000 and a M_w/M_n of 1.24, and the GPC curve thereof showed a single symmetrical peak.

(2) Synthesis of tri-block copolymer of B-A-B type

Under protection of N_2 , 5.33 g (0.071 mmol) of poly(poly(ethylene glycol) methacrylate), 30.41 mg (0.141 mmol) of ferrous bromide, 24.50 mg (0.141 mmol) of PMDETA, 13.41 g (0.197 mmol) of methyl acrylate and 15ml of toluene were blended to form a reaction system. Then the reaction system was sealed, and after 10 min of stirring, the reaction temperature was raised to 110 °C. Polymerization was carried out for 10 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through

Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted monomers and purified white powder of tri-block copolymer (B-A-B type) was obtained. The tri-block copolymer had a M_n of 170000 and a M_w/M_n of 1.43, and the GPC curve thereof showed a single symmetrical peak.

(3) Synthesis of penta-block copolymer of A-B-A-B-A type

Under argon atmosphere, 13.10 mg (0.09 mmol) of CuBr and 28.52 mg (0.18 mmol) of bpy were added to 8 ml of toluene to form a reaction system. After 10 min of stirring, a catalyst/ligand complex was formed. 8.28 g (3.6 mmol) of poly(ethylene glycol) methacrylate ($M_n=2300$, $m=50$) was added and dissolved with stirring for 15 min. Then 1.31 g (0.018 mmol) of macromolecular initiator of tri-block copolymer prepared in Example 6-(2) was added into the reaction system. Then the reaction system was sealed, and after the tri-block copolymer was dissolved completely, the reaction temperature was raised to 90°C in a rate of 1.5°C/min. Polymerization was carried out for 100 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified white powder of poly(poly(ethylene glycol) methacrylate)-b-poly(methyl acrylate)-b-poly(poly(ethylene glycol) methacrylate)-b-poly(methyl acrylate)-b-poly(poly(ethylene glycol) methacrylate) penta-block copolymer (A-B-A-B-A type) was obtained. The penta-block copolymer had a M_n of 430000 and a M_w/M_n of 1.48, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 77.9 wt%.

(4) Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of the dried penta-block copolymer was dissolved in 15 ml of NMP, and 0.05 g of LiTFSI (the amount of added Li salt is 1 mol% relative to polyoxyethylene repeating unit) was added into the solution. Then the solution was sealed in a conical flask and stirred over 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the obtained polymer solid electrolyte membrane

was 50 μm .

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no crystallinity.

According to the results of DMA, the initial modulus of the polymer solid electrolyte membrane was 1.9 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be $5.3 \times 10^{-4} \text{ S/cm}$ by measuring at 23°C using electrochemical workstation.

Example 7 (Preparation of penta-block copolymer of A-B-A-B-A type and corresponding polymer solid electrolyte, in which poly(poly(ethylene glycol) phenoxy acrylate) was used as segment A and poly(4-methyl phenyl-3-octylene) was used as segment B)

(1) Synthesis of segment A

To 10 ml of toluene, 9.60 g of poly(ethylene glycol) phenoxy acrylate ($M_n=240$, $m=2$, 40.0 mmol) was added and dissolved under N_2 atmosphere. Then 57.34 mg (0.40 mmol) of CuBr and 107.82 mg (0.80 mmol) of bpy were added into the solution. After 10 min of stirring, 58.8 mg (0.40 mmol) of dichlorobenzene was added and heated to 90°C . After polymerization for 45 hours, the solution was cooled immediately in ice/water bath to stop the polymerization. Then, the solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified poly(poly(ethylene glycol) phenoxy acrylate) was obtained. The poly(poly(ethylene glycol)phenoxy acrylate) had a M_n of 11000 and a M_w/M_n of 1.15, and the GPC curve thereof showed a single symmetrical peak.

(2) Synthesis of tri-block copolymer of B-A-B type

Under protection of N_2 , 0.78 g (0.071 mmol) of poly(poly(ethylene glycol)

phenoxy acrylate), 20.28 mg (0.141 mmol) of CuBr, 24.50 mg (0.141 mmol) of PMDETA, 14.27 g (0.197 mmol) of 4-methyl phenyl-3-octylene and 15ml of toluene were blended to form a reaction system. Then the reaction system was sealed, and after 10 min of stirring, the reaction temperature was raised to 110°C. Polymerization was carried out for 10 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with n-hexane to remove unreacted monomers and purified white powder of tri-block copolymer (B-A-B type) was obtained. The tri-block copolymer had a M_n of 48000 and a M_w/M_n of 1.39, and the GPC curve thereof showed a single symmetrical peak.

(3) Synthesis of penta-block copolymer of A-B-A-B-A type

Under argon atmosphere, 13.10 mg (0.09 mmol) of CuBr and 28.52 mg (0.18 mmol) of bpy were added to 3 ml of toluene to form a reaction system, and after 10 min of stirring, a catalyst/ligand complex was formed. 1.73 g (7.2 mmol) of poly(ethylene glycol) phenoxy acrylate ($M_n=240$, $m=2$) was added and dissolved with stirring for 15 min. Then 0.86 g (0.018 mmol) of macromolecular initiator of the tri-block copolymer prepared in Example 7-(2) was added into the reaction system. Then the reaction system was sealed and after the tri-block copolymer was dissolved completely, the reaction temperature was raised to 90°C in a rate of 1.5°C/min. Polymerization was carried out for 100 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al₂O₃ column to remove catalyst/ligand. After removal of solvent, the reaction product was washed with diethyl ether anhydrous to remove unreacted monomers and purified white powder of poly(poly(ethylene glycol) phenoxy acrylate)-b-poly(4-methyl phenyl-3-octylene)-b-poly(poly(ethylene glycol) phenoxy acrylate)-b- Poly(4-methyl phenyl-3-octylene)-b-poly(poly(ethylene glycol) phenoxy acrylate) penta-block copolymer (A-B-A-B-A type) was obtained. The penta-block copolymer had a M_n of 83000 and a M_w/M_n of 1.54, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 55.4 wt%.

(4) Preparation of polymer solid electrolyte membrane and estimation of

properties

1 g of the dried penta-block copolymer was dissolved in 15 ml of NMP, and 0.02 g of LiCF_3SO_3 (the amount of added Li salt is 1 mol% relative to polyoxyethylene repeating unit) was added into the solution. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C . The thickness of the obtained polymer solid electrolyte membrane was $50\text{ }\mu\text{m}$.

The phase morphology of the membrane was observed by TEM and it showed co-continuous phase morphology.

According to the results of DSC, no melting peak was observed for the polymer solid electrolyte, and this fact meant that the polymer solid electrolyte had no crystallinity.

According to the results of DMA, the initial modulus of the polymer solid electrolyte membrane was 3.1 MPa.

The membrane was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be $9.2 \times 10^{-4}\text{ S/cm}$ by measuring at 23°C using electrochemical workstation.

Comparative Example 1 (Preparation of penta-block copolymer of A-B-A-B-A type, in which polyoxyethylene was used as segment A and PS was used as segment B)

(1) Synthesis of segment A

Under N_2 atmosphere, 120# gasoline was added firstly and then 0.42 g (2.04 mmol) of aluminiumisopropoxide as a catalyst was added with stirring. Then a toluene solution containing 8.81g (0.2 mol) of ethylene oxide was added into the catalyst solution. Polymerization was carried for 4 hours at 15°C and then 3 hours at 40°C . After polymerization, solvent was removed and the product solution was filtrated. Purified polyoxyethylene crystal which was grown during cooling process was obtained. The polyoxyethylene crystal had a M_n of 6000 and a M_w/M_n of 1.14, and the GPC curve thereof showed a single symmetrical peak.

By hydrolysis reaction, polyoxyethylene having hydroxyl groups in both terminals can be prepared.

By reaction of hydroxyl group and acyl bromide, polyoxyethylene having bromine groups in both terminals can be prepared.

(2) Synthesis of tri-block copolymer of B-A-B type

Under protection of N_2 , 0.43 g (0.071 mmol) of polyoxyethylene, 20.28 mg (0.141 mmol) of CuBr, 24.50 mg (0.141 mmol) of PMDETA, 20.56 g (0.197 mmol) of St were blended to form a reaction system. Then the reaction system was sealed, and after 10 min of stirring, the reaction temperature was raised to 110°C. Polymerization was carried out for 5 hours. Then the reaction system was cooled immediately in ice/water bath to stop the polymerization. The solution was diluted with THF and purified by passing through Al_2O_3 column to remove catalyst/ligand. After removal of solvent, the product was washed with n-hexane to remove unreacted monomers and purified white powder of tri-block copolymer (B-A-B type) was obtained. The tri-block copolymer had a M_n of 51000 and a M_w/M_n of 1.25, and the GPC curve thereof showed a single symmetrical peak.

(3) Synthesis of penta-block copolymer of A-B-A-B-A type

Commercially available poly(ethylene glycol) methyl ether with one hydroxyl group ($M_n=4000$) and the tri-block copolymer prepared in Comparative Example 1-(2) were dissolved in THF, and HBr was eliminated under high temperature of 130°C. After purification, purified penta-block copolymer (A-B-A-B-A type) was obtained. The penta-block copolymer had a M_n of 59000 and a M_w/M_n of 1.29, and the GPC curve thereof showed a single symmetrical peak, and the content of segment A (f_A) was 23.7 wt%.

(4) Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of the dried penta-block copolymer was dissolved in 15 ml of NMP, and after dissolving completely, the solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the obtained polymer solid electrolyte membrane was 40 μm .

The phase morphology of the membrane was observed by TEM and it showed lamellar phase morphology.

According to the results of DSC, the polymer solid electrolyte had a crystallinity of

12.3%.

Comparative Example 2 (Preparation of di-block copolymer of A-B type and corresponding polymer electrolyte, in which P(PEGMA) was used as segment A and PS was used as segment B)

(1) Synthesis of segment A

The segment A was synthesized as in Example 1 (1).

(2) Synthesis of di-block copolymer of A-B type

The di-block copolymer of A-B type was synthesized as in Example 1 (2).

By adjustment of feeding amount and reaction time, di-block copolymers with $f_A=10\sim70$ wt% were prepared.

Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of the dried di-block copolymer was dissolved in 15 ml of NMP, and LiTFSI was added, into the solution, in a ratio of 10 mol% of polyoxyethylene repeating unit. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C. The thickness of the obtained polymer solid electrolyte membrane was 40-50 μm .

The phase morphology of the membrane was observed by TEM and no micro-phase morphology was observed.

According to the results of DSC, polymer solid electrolytes with $f_A=10\sim70$ wt% varied in a crystallinity range of 2~24.6%.

According to the results of DMA, when $f_A=54.4$ wt%, the initial modulus of the polymer solid electrolyte membrane was 0.8 MPa.

A polymer solid electrolyte membrane with $f_A=54.4$ wt% was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be 3.6×10^{-6} S/cm by measuring at 23°C using electrochemical workstation.

Comparative Example 3 (Preparation of tri-block copolymer of A-B-A type and corresponding polymer electrolyte, in which P(PEGMA) was used as segment A

and PS was used as segment B)

(1) Synthesis of segment A

The segment A was synthesized as in Example 3 (1).

(2) Synthesis of tri-block copolymer of B-A-B type

The tri-block copolymer of B-A-B type was synthesized as in Example 3 (2).

By adjustment of feeding amount and reaction time, tri-block copolymers with $f_A=10\sim80$ wt% were prepared.

(3) Preparation of polymer solid electrolyte membrane and estimation of properties

1 g of dried tri-block copolymer was dissolved in 15 ml of NMP, and LiTFSI was added, into the solution, in a ratio of 10 mol% of polyoxyethylene repeating unit. Then the solution was sealed in a conical flask and stirred for 24 hours. The solution was casted on a silica wafer and the solvent was removed under 60°C . The thickness of the obtained polymer solid electrolyte membrane was 25-50 μm .

The phase morphology of the membrane was observed by TEM. The membrane had co-continuous phase morphology and its f_A was in ranges of 20~25 wt% and 60~65 wt%. Polymer solid electrolytes having f_A outside the above ranges had “sea-island” or lamellar phase morphology.

According to the results of DSC, polymer solid electrolytes with $f_A=10\sim80$ wt% varied in a crystallinity range of 0.7~21.5%.

According to the results of DMA, when $f_A=23.7$ wt%, the initial modulus of the polymer solid electrolyte membrane was 1.2 MPa.

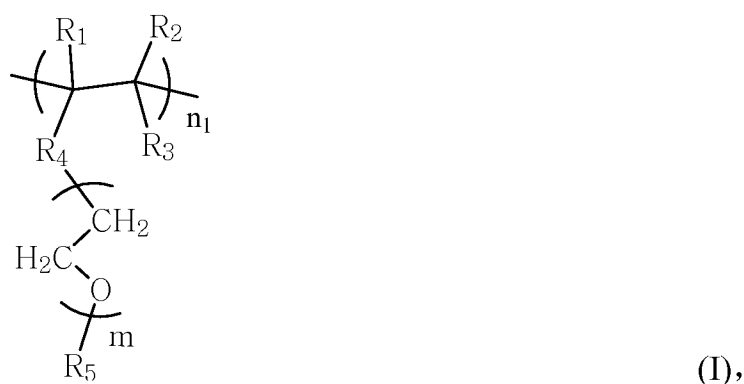
A polymer solid electrolyte Membrane with $f_A=23.7$ wt% was put into a glove box for more than one week to completely remove water or solvent, and then assembled in a UFO cell. The lithium ion conductivity was found to be 1.9×10^{-5} S/cm by measuring at 23°C using electrochemical workstation.

Claims

1. A multi-block copolymer of formula (P1) comprising segment A having polyoxyethylene repeating unit in the side chain thereof, and segment B having no polyoxyethylene repeating unit; n is a positive integer; and when $n \geq 2$, a and b are independently 0 or 1, and when $n=1$, $a=b=1$.



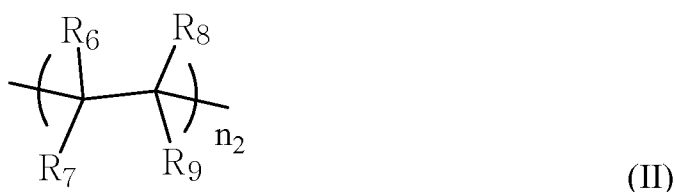
2. The multi-block copolymer according to claim 1, wherein the structure of the segment A is shown as formula (I):



wherein $R_1 \sim R_3$ are independently H or C1~C10 alkyl, R_4 is $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ or $-\overset{\text{H}_2}{\text{C}}-\text{C}_6\text{H}_4-$, R_5 is H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-hexyl, or phenyl, m is an integer of 2 to 50, and n_1 is an integer of 10 to 500.

3. The multi-block copolymer according to claim 2, wherein $R_1 \sim R_3$ are independently H, methyl or ethyl, R_4 is $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ or $-\overset{\text{H}_2}{\text{C}}-\text{C}_6\text{H}_4-$, R_5 is H, methyl or ethyl, m is an integer of 5 to 30, and n_1 is an integer of 20 to 300.

4. The multi-block copolymer according to any one of claims 1 to 3, wherein the structure of the segment B is shown as formula (II):



wherein $R_6 \sim R_8$ are independently H or C1~C10 alkyl, R_9 is phenyl, p-methylphenyl, m-methyl styrene, p-fluorophenyl, nitrile or carbomethoxy, n_2 is an integer of 10 to 500.

5. The multi-block copolymer according to claim 4, wherein $R_6 \sim R_8$ are independently H, methyl or ethyl, R_9 is phenyl, p-methylphenyl or carbomethoxy, n_2 is an integer of 20 to 300.
6. The multi-block copolymer according to any one of claims 1 to 5, wherein the multi-block copolymer has co-continuous phase separation morphology.
7. A polymer electrolyte material comprising the multi-block copolymer according to claim 1 and an electrolyte salt.
8. The polymer electrolyte material according to claim 7, wherein the polymer electrolyte material has co-continuous separation morphology.
9. The polymer electrolyte material according to claim 8, wherein the electrolyte salt is a lithium salt.
10. The polymer electrolyte material according to claim 9, wherein the lithium salt is selected from the group consisting of lithium bis(trifluoromethane sulfonimide) (LiTFSI), lithium perchlorate (LiClO_4), lithium tri-fluoromethanesulfonate (LiCF_3SO_3), lithium hexa-fluorophosphate (LiPF_6), lithium tetra-fluoroborate (LiBF_4), and mixtures thereof.

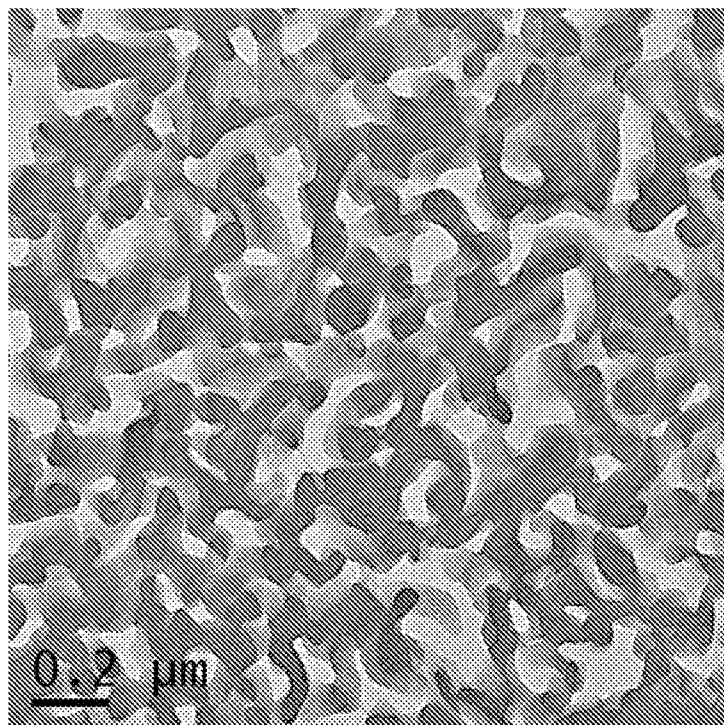


Figure 1

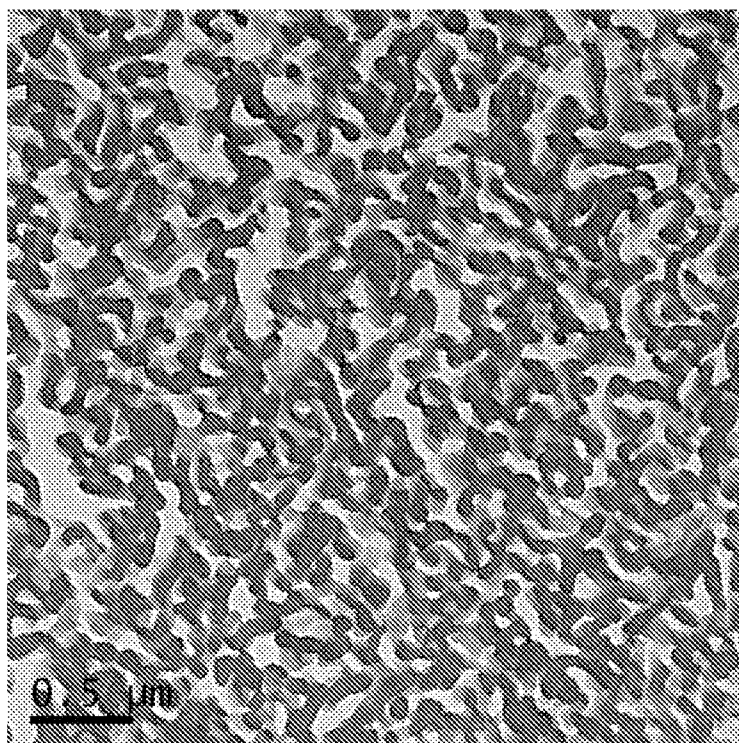


Figure 2

- 2/2 -

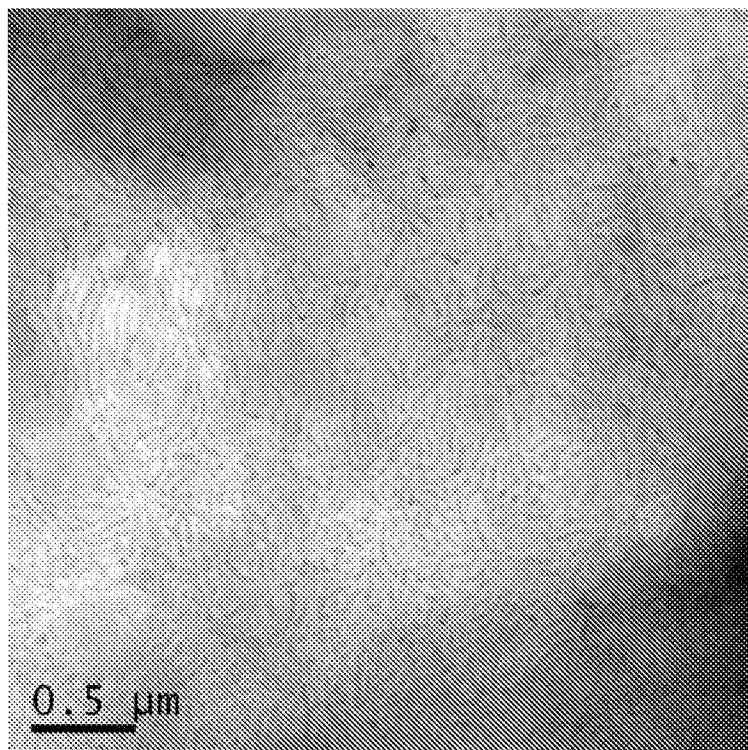


Figure 3

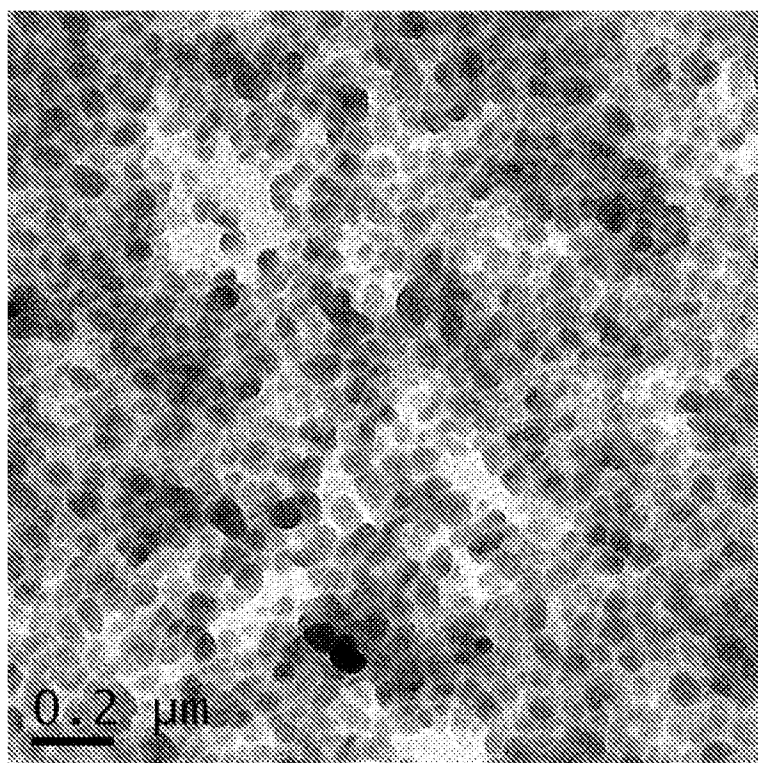


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2013/089237

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08F 297/-; H01M 10/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, CNTXT, DWPI, SIPOABS, WOTXT, CNKI, GOOGLE: electrolyte?, battery, +block???, co?polymer?, poly+, +oxyethylene+, +ethylene glycol, +acrylate+, +allyl+, styrene, acrylonitrile, side+ +chain, lithium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010221614 A1 (ARKEMA etc.) 02 September 2010 (02.09.2010) claims 1, 9, 21	1-10
Y	US 5374495 A (SONY CORP) 20 December 1994 (20.12.1994) abstract, description, column 3, line 25 to column 4, line 10	1-10
Y	US 2012029099 A1 (SEEO INC) 02 February 2012 (02.02.2012) description, paragraph [0011]	1-10
Y	US 2005170286 A (EASTMAN KODAK CO etc.) 04 August 2005 (04.08.2005) claim 13	1-6
Y	CN 102375849 A (SHENZHEN BAK BATTERY CO LTD) 14 March 2012 (14.03.2012) description, paragraph [0043]	1-10
Y	CN 1178801 A (UNIV SICHUAN) 15 April 1998 (15.04.1998) claim 1	1-6

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
07 Mar. 2014(07.03.2014)Date of mailing of the international search report
20 Mar. 2014 (20.03.2014)Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China
100088
Facsimile No. 86-10-62019451Authorized officer
XUE, Haijiao
Telephone No. (86-10)62085466

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2013/089237

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CN 1178801 A	15.04.1998	None	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2013/089237

A. CLASSIFICATION OF SUBJECT MATTER

C08F 297/06 (2006.01) i

H01M 10/02 (2006.01) i