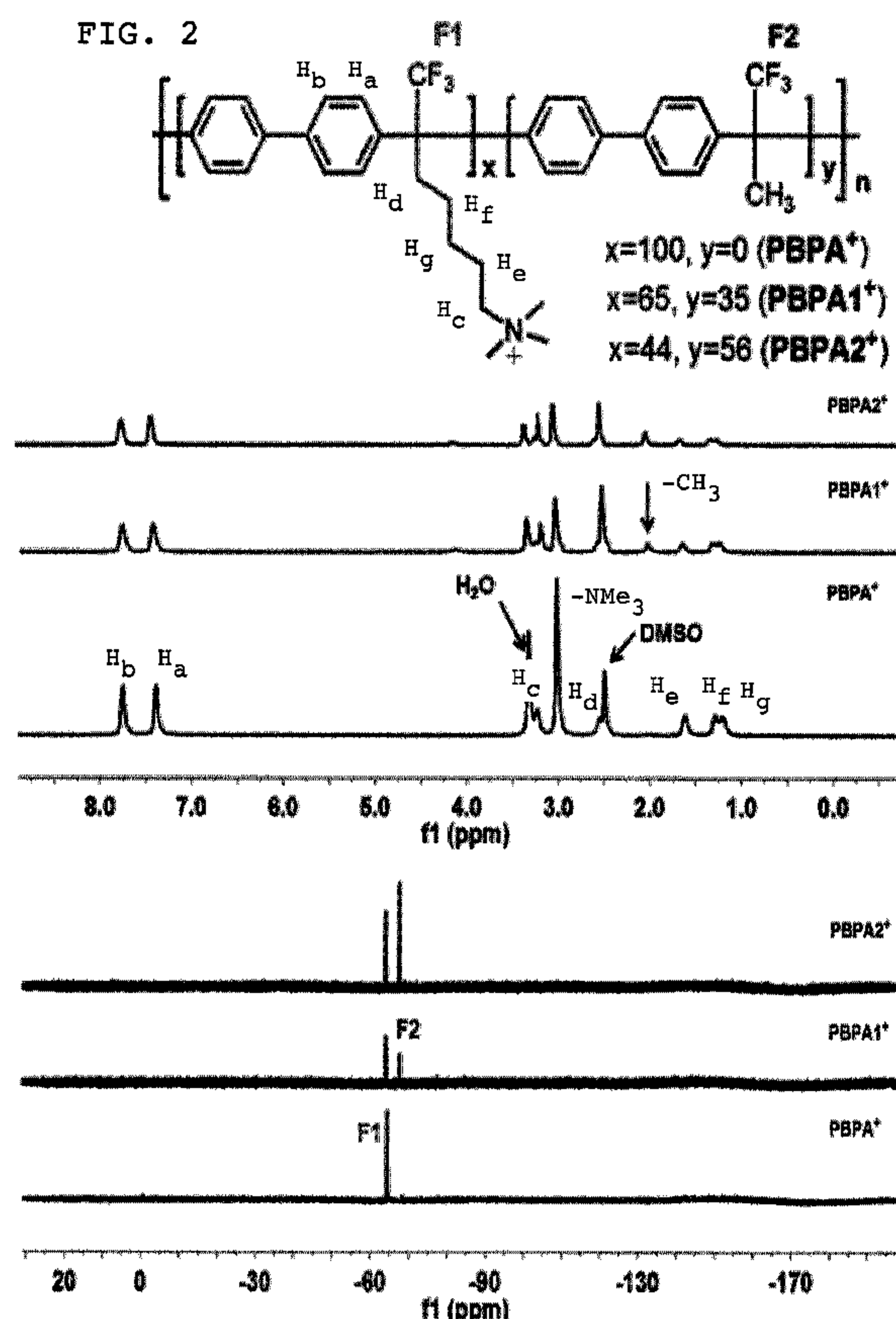




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(54) **Titre : NOUVEAUX POLYMERES ET PROCEDES DE FABRICATION DESDITS POLYMERES**
(54) **Title: NOVEL POLYMERS AND METHODS FOR THEIR MANUFACTURE**



(57) **Abrégé/Abstract:**

Embodiments of the invention relate to a novel class of polymers with superior mechanical properties and chemical stability, as compared to known polymers. These polymers are particularly well suited for use in anion exchange membranes (AEMs), including those employed in fuel cells. Novel methods for the manufacture of these polymers are also described.

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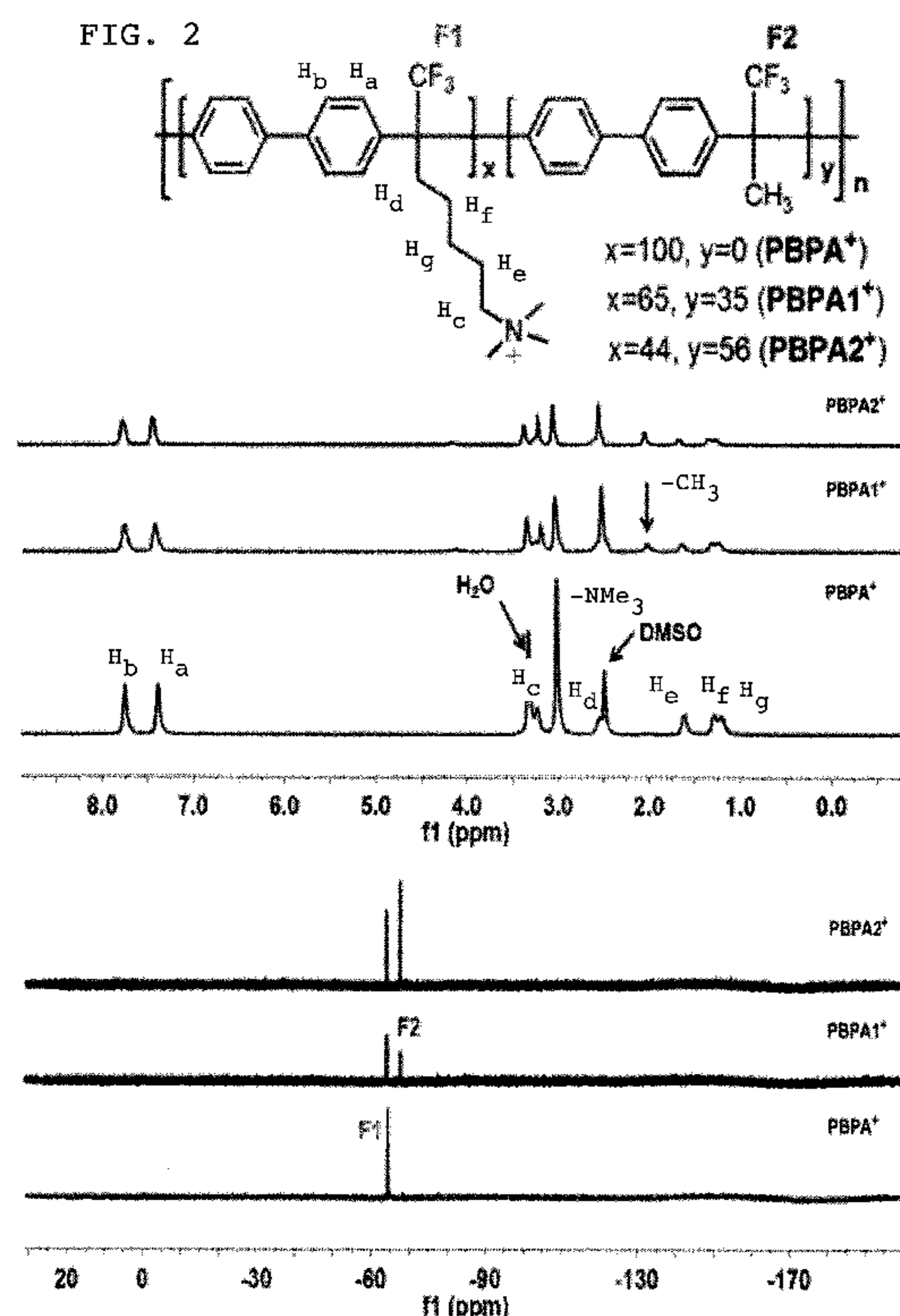
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(54) Title: NOVEL POLYMERS AND METHODS FOR THEIR MANUFACTURE



(57) Abstract: Embodiments of the invention relate to a novel class of polymers with superior mechanical properties and chemical stability, as compared to known polymers. These polymers are particularly well suited for use in anion exchange membranes (AEMs), including those employed in fuel cells. Novel methods for the manufacture of these polymers are also described.

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1 NOVEL POLYMERS AND METHODS FOR THEIR MANUFACTURE

2
3 CROSS-REFERENCE TO RELATED APPLICATIONS

4 This application claims the benefit of co-pending US Provisional Patent
5 Application Serial No. 62/081,144, filed 18 November 2014, which is hereby
6 incorporated herein as though fully set forth.

7
8 BACKGROUND

9 Alkaline exchange membranes or anion exchange membranes (AEMs) allow for
10 the transportation of anions (e.g., OH⁻, Cl⁻, Br⁻) from the cathode to the anode in an
11 electrochemical reaction. AEMs are a critical component of AEM fuel cells, where
12 hydrogen and oxygen are used to generate electricity, with water as a byproduct.
13 AEMs are also used in water electrolysis, where water is split into hydrogen and
14 oxygen using electricity. In both AEM fuel cells and water electrolysis, hydroxide
15 ions (OH⁻) are transported through the AEM, along with water molecules. AEMs may
16 also be used, for example, in batteries, sensors, and as actuators.

17 Known AEMs are generally unsuitable for use in AEM fuel cells or water
18 electrolysis. Many commercially-available AEMs are based on polystyrene, which is
19 generally considered a poor choice for AEM fuel cells or water electrolysis.

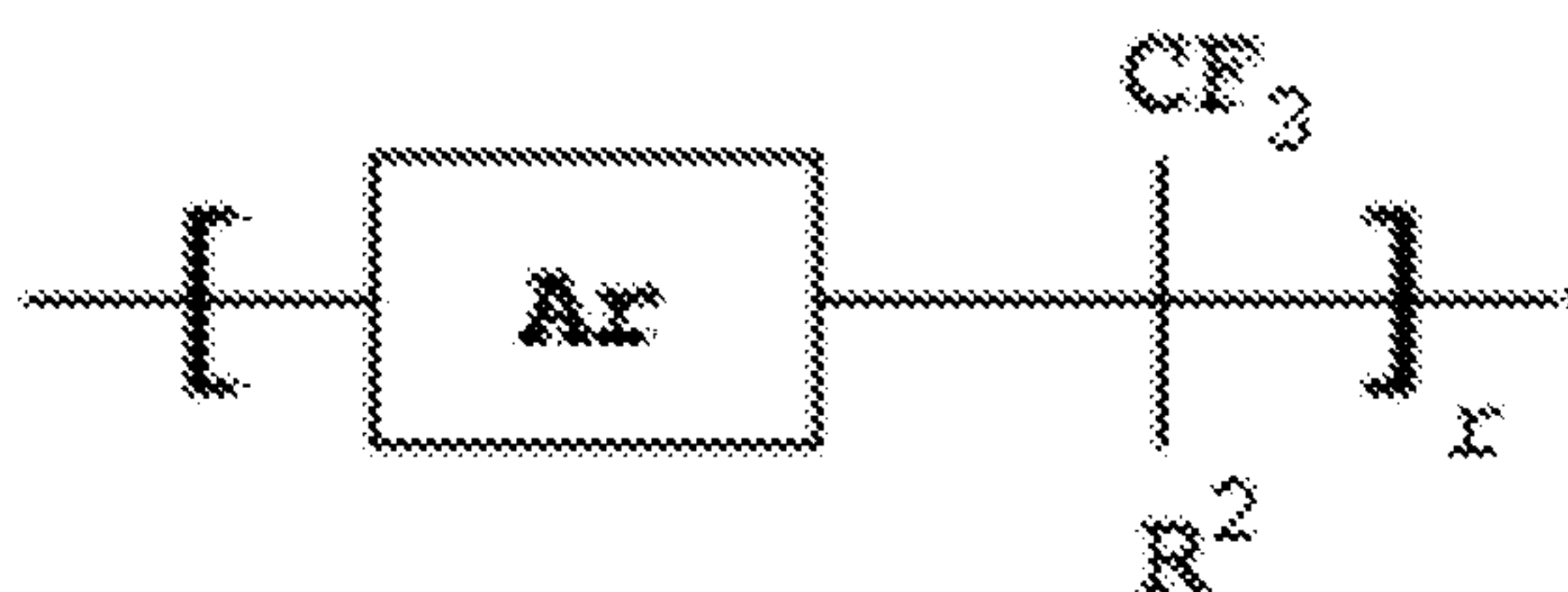
20 Other AEM materials include polysulfones, poly(phenylene oxide)s,
21 poly(phenylene)s, poly(benzimidazolium)s, poly(arylene ether ketone)s, and
22 poly(arylene ether sulfone)s. These polymers contain an arylene ether linkage (—O—)
23 in the mid-chain and a benzyltrimethyl ammonium group in the side-chain. This
24 combination, however, has been found to be chemically unstable and to degrade
25 easily under highly alkaline conditions. Known polyarylenes, in particular, will
26 contain ether linkages in the polymer backbone because they are typically synthesized
27 by basic condensation reactions between diol monomers and dihalide monomers,
28 which produces hydrogen chloride as a byproduct.

29 In addition, the chloromethylation reaction involved in the manufacture of these
30 polymers requires the use of toxic reagents, long reaction times, and extensive
31 optimization to reach a desired degree of functionalization. Side reactions (e.g.,
32 gelation) frequently occur over prolonged reaction times, making it difficult to
33 achieve an ion-exchange capacity (IEC) above 2.5 mequiv/g.

BRIEF DESCRIPTION OF THE INVENTION

In one embodiment, the invention provides a method of forming a polymer, the method comprising: reacting an aromatic compound and a trifluoroalkyl ketone in the presence of a strong acid to form a bromoalkylated precursor polymer; and reacting the bromoalkylated precursor polymer with a trialkylamine and sodium hydroxide to form a polyarylene having a main chain free of ether linkages.

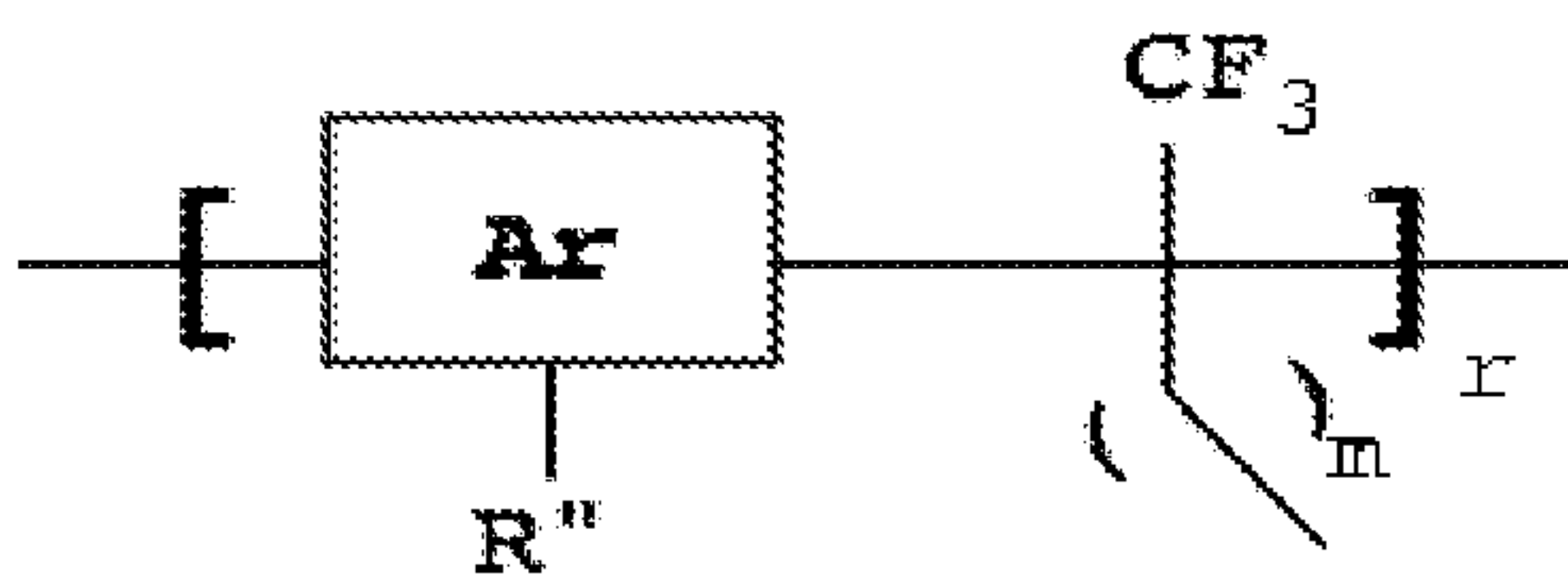
In another embodiment, the invention provides a polymer according to formula I (formula I), wherein Ar is an aromatic compound, r is from 100 to 1,000,000, R² is



, R is an alkyl group, and n is from 1

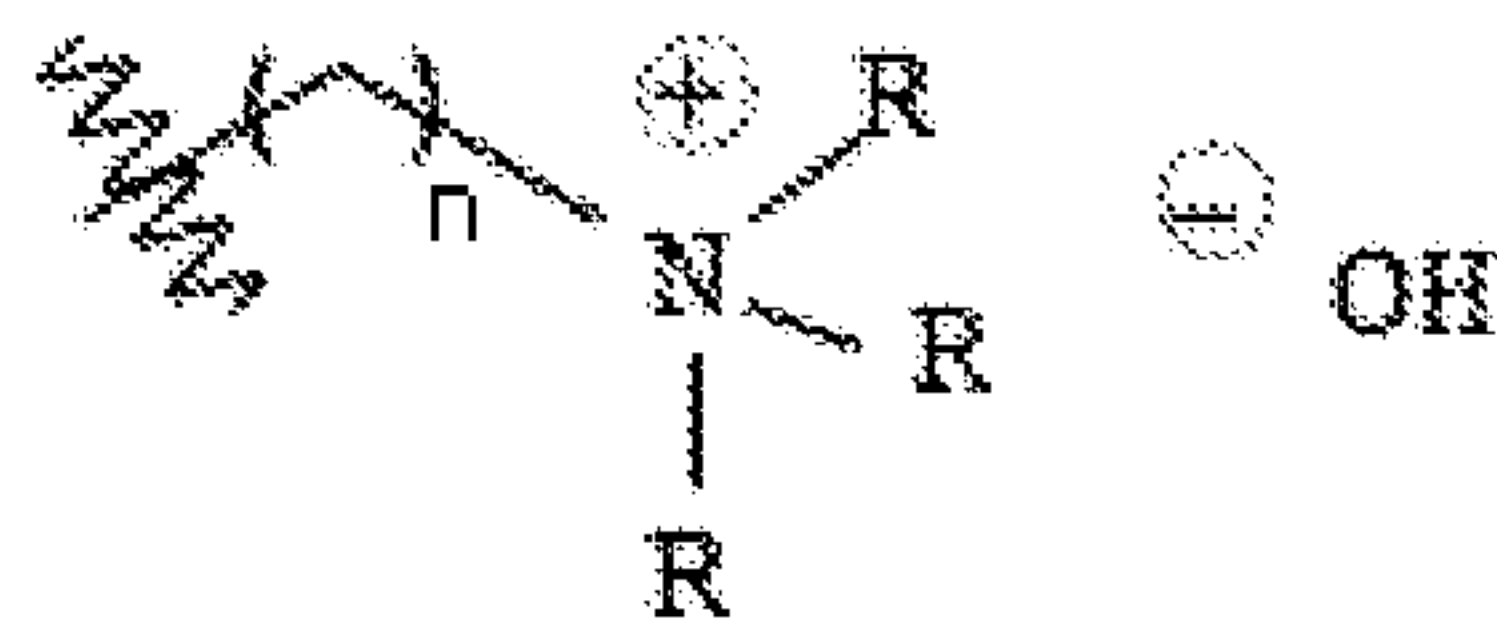
to 20.

In still another embodiment, the invention provides polymer according to formula III



(formula III), wherein Ar is an aromatic

compound, R" is



, r is from 100 to 1,000,000, and m

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features of this invention will be more readily understood from the following detailed description of the various aspects of the invention taken in conjunction with the accompanying drawings that depict various embodiments of the invention, in which:

FIG. 1 shows ¹H and ¹⁹F NMR spectra of three illustrative bromoalkylated precursor polymers according to embodiments of the invention;

FIG. 2 shows ¹H and ¹⁹F NMR spectra of three illustrative polyarylenes according to embodiments of the invention;

FIG. 3 shows ^1H NMR spectra of the three polyarylenes of FIG. 2 before and after alkaline stability tests;

FIG. 4 shows a ^1H NMR spectrum of one of the three polyarylenes of FIG. 2 before and after an alkaline stability test; and

FIG. 5 shows (a) stress and strain curves of three polyarylenes according to embodiments of the invention and (b) H_2/O_2 polarization, high-frequency resistance, and power density curves of one of the three polyarylenes.

It is noted that the drawings of the invention are not to scale. The drawings are intended to depict only typical aspects of the invention, and therefore should not be considered as limiting the scope of the invention.

DETAILED DESCRIPTION

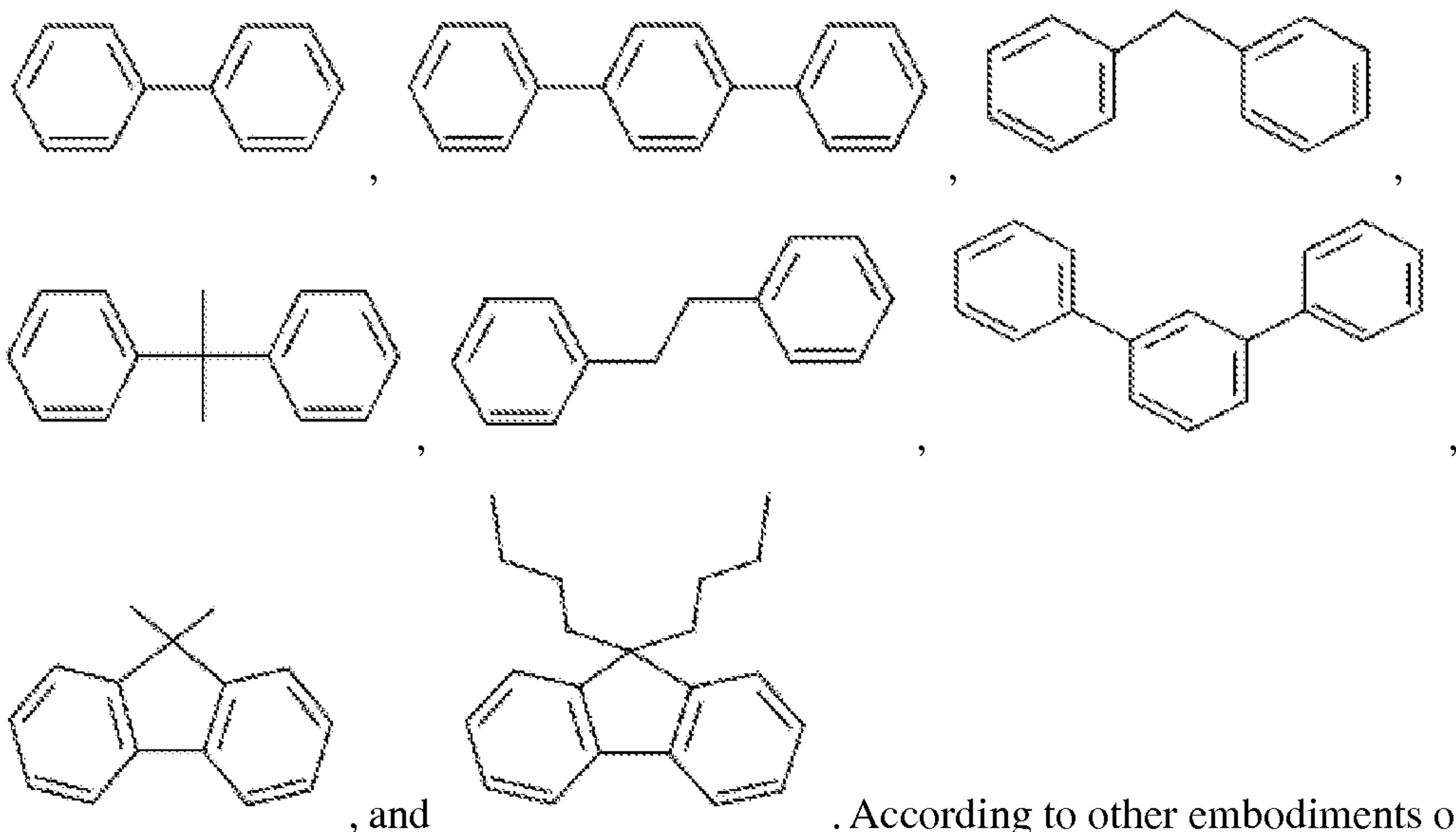
Some embodiments of the invention relate to a novel class of quaternized ammonium hydroxide-containing polyarylene polymers and methods for their manufacture. Applicants have, for the first time, manufactured high molecular weight, quaternary ammonium-tethered polyarylenes (including poly(biphenyl alkylene)s) without alkaline labile C–O bonds using acid-catalyzed polycondensation reactions.

In addition to their use in AEMs in the fuel cell and water electrolysis contexts noted above, Applicants have also found polymers of the invention to be useful in metal–air battery technologies. Surprisingly, Applicants have also found that these polymers exhibit antimicrobial activity, making them potentially useful as antimicrobial coatings for any number of products.

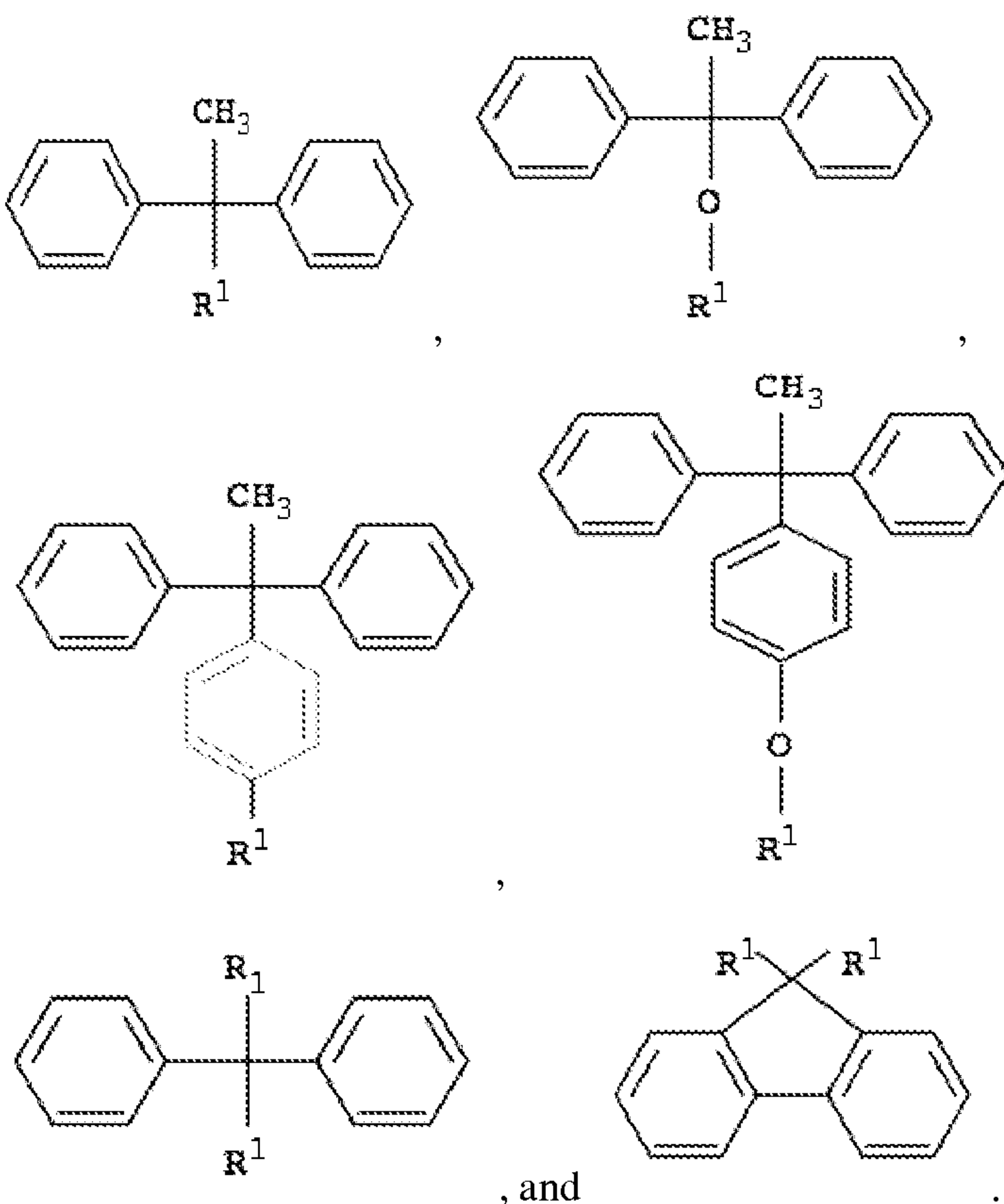
As will be explained in greater detail below, the polymers of the invention are synthesized by acidic condensation between ketone and aromatic compounds. As a result, the byproduct is water, rather than hydrogen chloride, as in known polyarylene synthesis methods.

Applicants have developed a novel method of polymer manufacture, generally comprising: reacting an aromatic compound and a trifluoroalkyl ketone in the presence of a strong acid (acid-catalyzed Friedel–Crafts polycondensation) to form a bromoalkylated precursor polymer; and reacting the bromoalkylated precursor polymer with a trialkylamine in the presence of sodium hydroxide to form a polyarylene having a main chain free of ether linkages.

According to some embodiments of the invention, the aromatic compound is selected from a group consisting of:



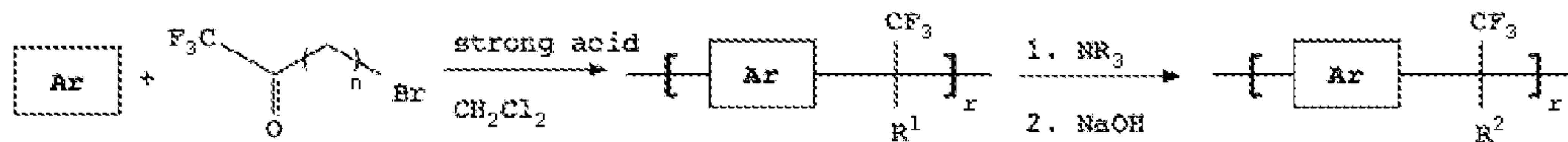
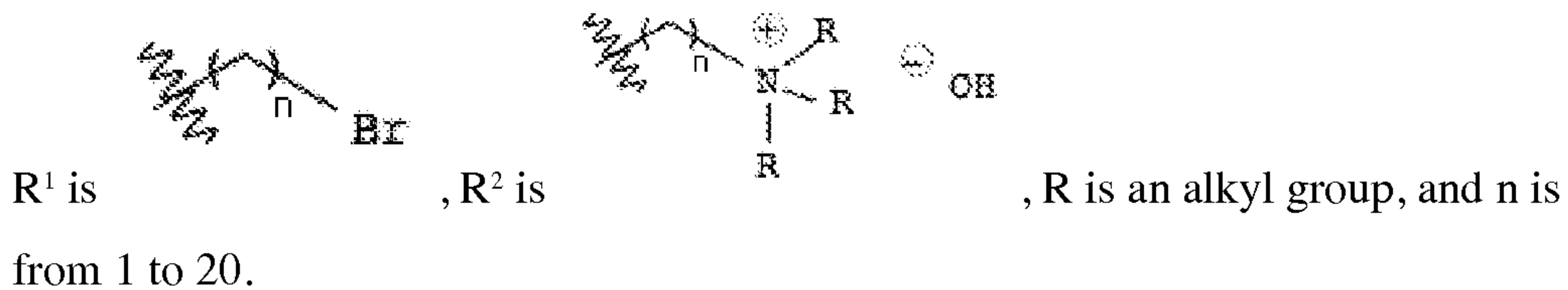
. According to other embodiments of the invention, the aromatic compound is selected from a group consisting of:



. In some particular embodiments of the invention, the aromatic compound is biphenyl.

According to some embodiments of the invention, the trifluoroalkyl ketone is selected from a group consisting of: 7-bromo-1,1,1-trifluoroheptan-2-one and methyl trifluoromethyl ketone.

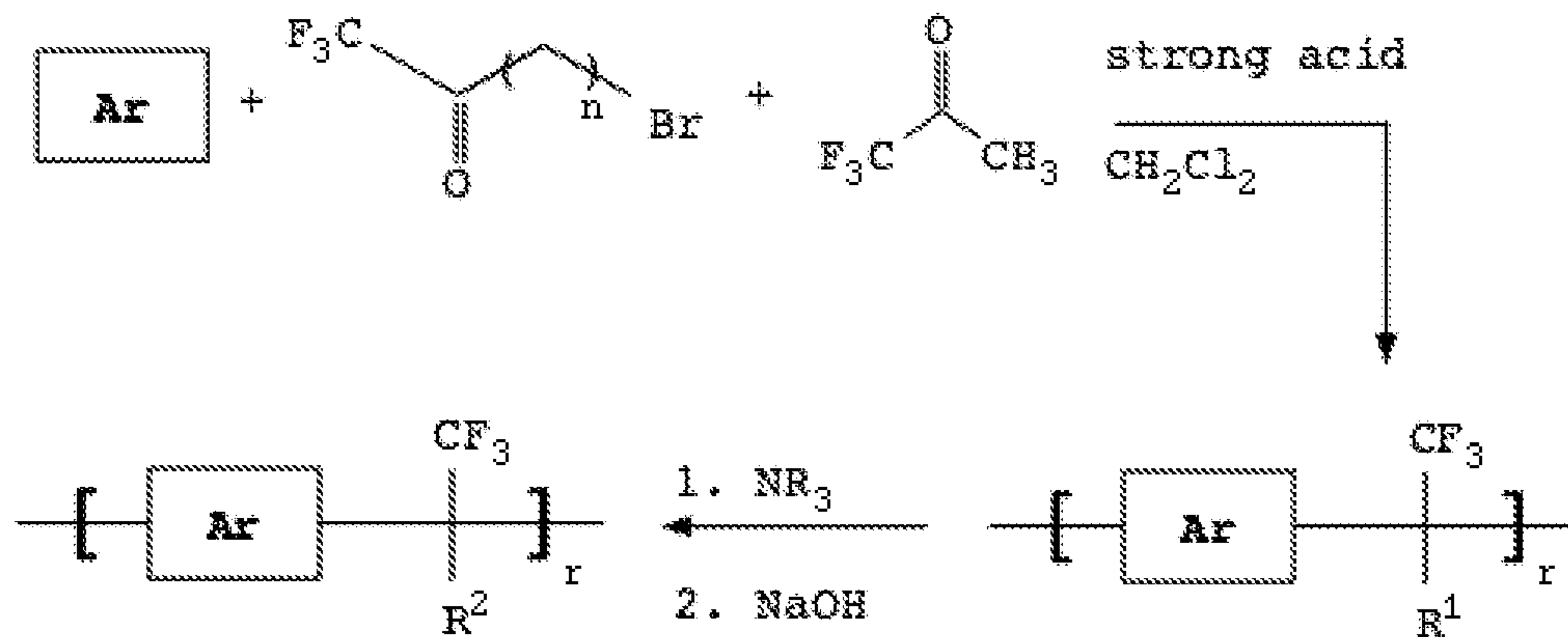
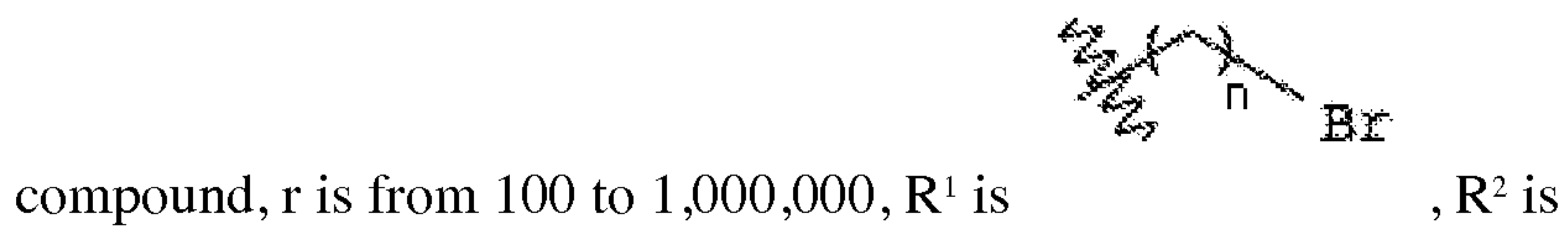
According to some embodiments of the invention, a polymer is manufactured according to Reaction 1 below, where Ar is a polyarylene, r is from 100 to 1,000,000,



(Reaction 1)

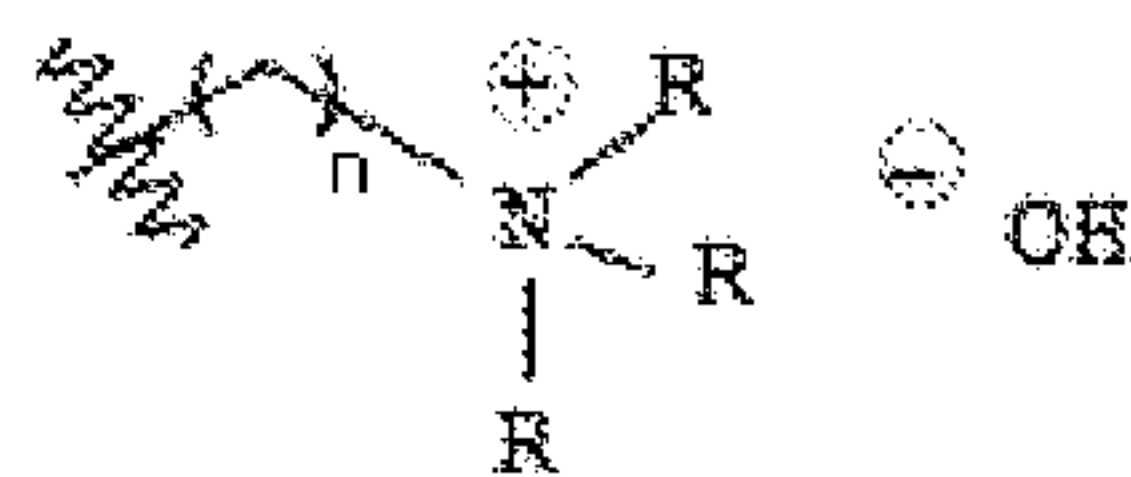
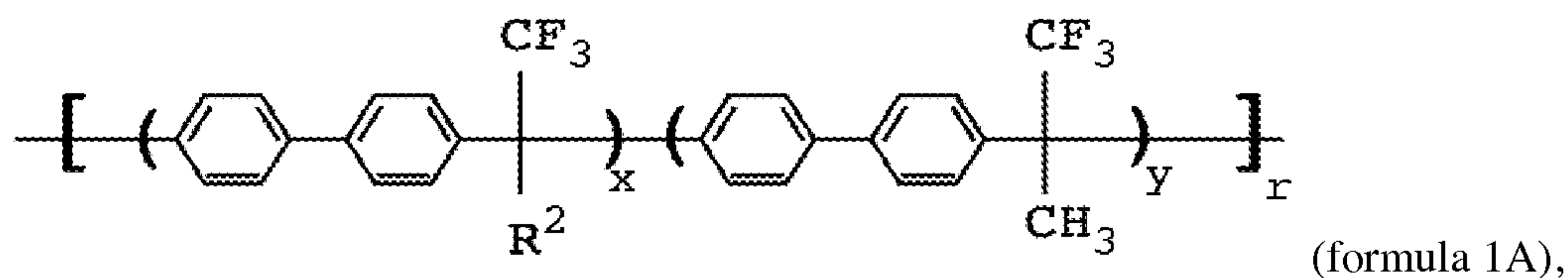
Strong acids suitable for use in Reaction 1 include trifluoromethane sulfonic acid, although other suitable acids will be apparent to one of ordinary skill in the art.

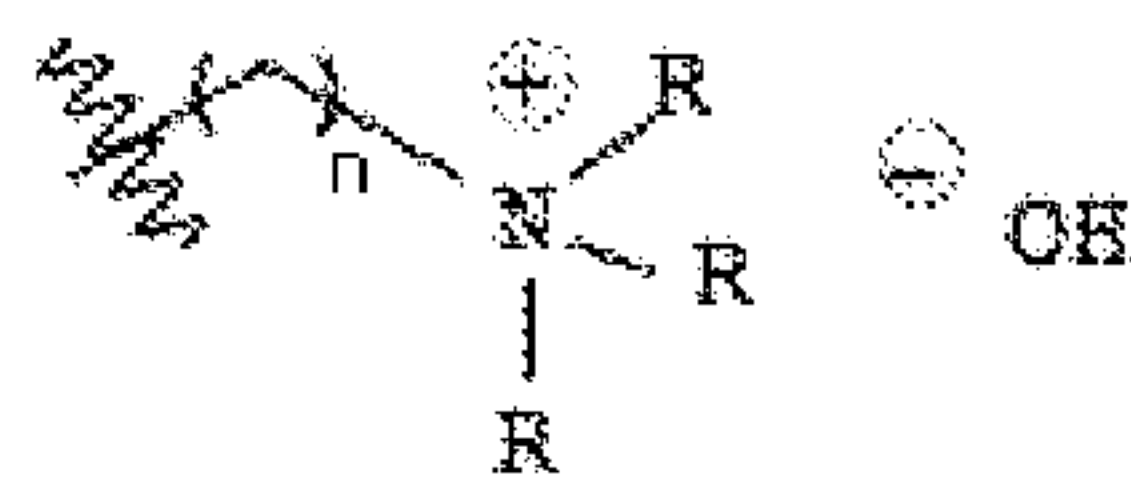
In other embodiments of the invention, an aromatic group may be combined with multiple trifluoroalkyl ketones, as in Reaction 1A below, where Ar is an aromatic



(Reaction 1A)

The manufacture of three exemplary poly(biphenyl alkylene)s according to embodiments of the invention is described below. These poly(biphenyl alkylene)s have general formula IA



where R^2 is , $x + y = 1$, and r is from 100 to 1,000,000. In a first poly(biphenyl alkylene), referred to as PBPA+, x is 1 and y is 0. In a second poly(biphenyl alkylene), referred to as PBPA1+, x is 0.65 and y is 0.35. In a third poly(biphenyl alkylene), referred to as PBPA2+, x is 0.44 and y is 0.56.

Example 1—PBPA+

Biphenyl (0.70 g, 4.53 mmol), 7-bromo-1,1,1-trifluoroheptan-2-one (1.12 g, 4.53 mmol), methylene chloride (3.0 mL), and trifluoromethanesulfonic acid (TFSA) were mixed under nitrogen at room temperature using a magnetic stirring bar. After 10 hours, the reaction mixture solution became highly viscous and was stirred for an additional two hours. The resulting dark brown, gel-like mass was then shredded with sonication and poured slowly into methanol, forming a white fiber, which was then filtered and washed with hot methanol. After vacuum drying, 1.70 g (97% yield) of a white fiber-like solid, a bromoalkylated precursor polymer referred to herein as PBPA, was obtained. FIG. 1 shows ^1H and ^{19}F NMR spectra of three bromoalkylated poly(biphenyl alkylene) precursors, including PBPA.

PBPA (200 mg) was dissolved in tetrahydrofuran (THF; 2 mL) and aqueous trimethylamine (1 mL) added to the solution, which was stirred at room temperature. The solubility of the polymer gradually decreased and the ionic polymer was precipitated after six hours. Deionized water (1 mL) was added to the solution to dissolve the precipitate. Addition of THF, stirring at RT for six hours, and dissolution with deionized water

1 was repeated. Volatile solven was then evaporated using a rotary
2 evaporator and the residue redissolved with a small amount of
3 methanol (approximately 2 mL). The ionic polymer was
4 precipitated by adding ether, filtered, and dried under vacuum,
5 resulting in a 97% yield (227 mg) of the poly(biphenyl alkylene)
6 PBPA+. FIG. 2 shows ¹H and ¹⁹F NMR spectra of three
7 poly(biphenyl alkylene)s, including PBPA+.

8
9 *Example 2—PBPA1+*

10 Biphenyl (0.70 g, 4.53 mmol), 7-bromo-1,1,1-
11 trifluoroheptan-2-one (0.73 g, 2.95 mmol), methyl
12 trifluoromethyl ketone (0.18 g, 1.60 mmol), methylene chloride
13 (3.0 mL), and TFSA (2.0 mL) were stirred under nitrogen at RT
14 using a magnetic stirring bar. After five hours, the reaction
15 mixture solution became highly viscous and was stirred for an
16 additional two hours. The resulting dark brown, gel-like mass
17 was then shredded with sonication and poured slowly into
18 methanol. A white fiber formed and was filtered and washed with
19 hot methanol. After drying under vacuum, 1.4 g (96% yield)
20 solid, a bromoalkylated precursor polymer referred to herein as
21 PBPA1, was obtained. FIG. 1 shows ¹H and ¹⁹F NMR spectra of
22 three bromoalkylated poly(biphenyl alkylene) precursors,
23 including PBPA1.

24 PBPA1 (200 mg) was dissolved in tetrahydrofuran (THF; 2
25 mL) and aqueous trimethylamine (1mL) added to the solution,
26 which was stirred at room temperature. The solubility of the
27 polymer gradually decreased and the ionic polymer was
28 precipitated after six hours. Deionized water (1 mL) was added
29 to the solution to dissolve the precipitate. Addition of THF,
30 stirring at RT for six hours, and dissolution with deionized water
31 was repeated. Volatile solven was then evaporated using a rotary
32 evaporator and the residue redissolved with a small amount of
33 methanol (approximately 2 mL). The ionic polymer was
34 precipitated by adding ether, filtered, and dried under vacuum,
35 resulting in a 98% yield (219 mg) of the poly(biphenyl alkylene)

1 PBPA1+. FIG. 2 shows ^1H and ^{19}F NMR spectra of three
2 poly(biphenyl alkylene)s, including PBPA1+.

3
4 *Example 3—PBPA2+*

5 Biphenyl (0.50 g, 3.24 mmol), 7-bromo-1,1,1-
6 trifluoroheptan-2-one (0.40 g, 1.62 mmol), methyl
7 trifluoromethyl ketone (0.19 g, 1.69 mmol), methylene chloride
8 (2.5 mL), and TFSA (2.3 mL) were stirred under nitrogen at RT
9 using a magnetic stirring bar. After three hours, the reaction
10 mixture solution became highly viscous and was stirred an
11 additional two hours. The resulting dark brown, gel-like mass
12 was then shredded with sonication and poured slowly into
13 methanol. A white fiber formed and was filtered and washed with
14 hot methanol. After drying under vacuum, 0.94 g of a white
15 fiber-like solid, a bromoalkylated precursor polymer referred to
16 herein as PBPA2, was obtained. FIG. 1 shows ^1H and ^{19}F NMR
17 spectra of three bromoalkylated poly(biphenyl alkylene)
18 precursors, including PBPA2.

19 PBPA2 (200 mg) was dissolved in tetrahydrofuran (THF; 2
20 mL) and aqueous trimethylamine (1mL) added to the solution,
21 which was stirred at room temperature. The solubility of the
22 polymer gradually decreased and the ionic polymer was
23 precipitated after six hours. Deionized water (1 mL) was added
24 to the solution to dissolve the precipitate. Addition of THF,
25 stirring at RT for six hours, and dissolution with deionized water
26 was repeated. Volatile solvent was then evaporated using a rotary
27 evaporator and the residue redissolved with a small amount of
28 methanol (approximately 2 mL). The ionic polymer was
29 precipitated by adding ether, filtered, and dried under vacuum,
30 resulting in a 98% yield (210 mg) of the poly(biphenyl alkylene)
31 PBPA2+. FIG. 2 shows ^1H and ^{19}F NMR spectra of three
32 poly(biphenyl alkylene)s, including PBPA2+.

Table 1 below shows water uptake (WU) and anion conductivity data for the PBPA+, PBPA1+, and PBPA2+ polymers.

Ionic polymer	WU(%)		Cl ⁻ (mS/cm)			OH ⁻ (mS/cm)		
	30°C	80°C	30°C	60°C	80°C	30°C	60°C	80°C
PBPA⁺	130	145	23	49	68/65 ^a	62	94	122/124 ^a
PBPA1⁺	102	110	14	28	47/50 ^a	41	58	88/92 ^a
PBPA2⁺	70	76	7	14	24/22 ^a	15	23	35/35 ^a

^a After immersion to 1 M NaOH solution for 30 days.

All three polymers exhibited excellent WU and conductivity properties, particularly PBPA+. Despite these WU values, all three polymers exhibited low swelling ratios (40% for PBPA+, 10% for PBPA1+, and 5% for PBPA2+), likely due to the presence of a rigid aromatic backbone.

Table 2 below shows ion-exchange capacity (IEC) data in mequiv/g for the PBPA+, PBPA1+, and PBPA2+ polymers before and after alkaline stability testing.

Sample	before		After 80°C, 7day		After 80°C, 30day	
	¹ H NMR	titration	¹ H NMR	titration	¹ H NMR	titration
PBPA⁺	2.61	2.70 (± 0.1)	2.61	2.74 (± 0.1)	2.60	2.65 (± 0.03)
PBPA1⁺	1.91	1.94 (± 0.04)	1.89	1.94 (± 0.03)	1.93	1.92 (± 0.03)
PBPA2⁺	1.45	1.46 (± 0.01)	1.49	1.47 (± 0.03)	1.46	1.48 (± 0.01)

As can be seen from the data in Table 2, all three poly(biphenyl alkylene)s exhibited remarkable IEC stability in an alkaline environment (1M NaOH), even after an extended period. As should also be apparent from the results in Table 2 and the examples above, the IEC of the polymers may be controlled by adjusting the relative proportions of different trifluoroalkyl ketones.

Interestingly, PBPA1+ afforded significantly higher hydroxide ion conductivity than other reported aromatic AEMs with similar IECs (*e.g.*, quaternized poly(phenylene oxide)s, poly(arylene ether ketone)s, and poly(arylene ether sulfone)s). This is likely attributable to the relatively higher WU of PBPA1+, which helps the hydrated membrane diffuse hydroxide ions more effectively. All three polymers exhibit increased hydroxide ion conductivity with increasing temperature, primarily due to the faster migration of ions and higher diffusivity with increasing temperature.

FIG. 3 shows ^1H NMR spectra for PBPA+, PBPA1+, and PBPA2+ before and after the 30-day alkaline stability test (1M NaOH, 80 °C) described above in Table 2.

FIG. 4 shows ^1H NMR spectra data for PBPA+ following another alkaline test (1M NaOH, 100 °C, 30 days).

PBPA+, PBPA1+, and PBPA2+ are insoluble in water, tetrahydrofuran, trichloromethane (CHCl_3), and dichloroethene (CH_2Cl_2), but are soluble in *N,N*-dimethylformamide, dimethylsulfoxide, and methanol at room temperature. The quaternary ammonium groups of these polymers decomposed at 270 °C, a thermal stability greater than that reported for QA poly(arylene ether sulfone)s. The precursor polymers (PBPA, PBPA1, PBPA2) were thermally stable without decomposition up to 350 °C.

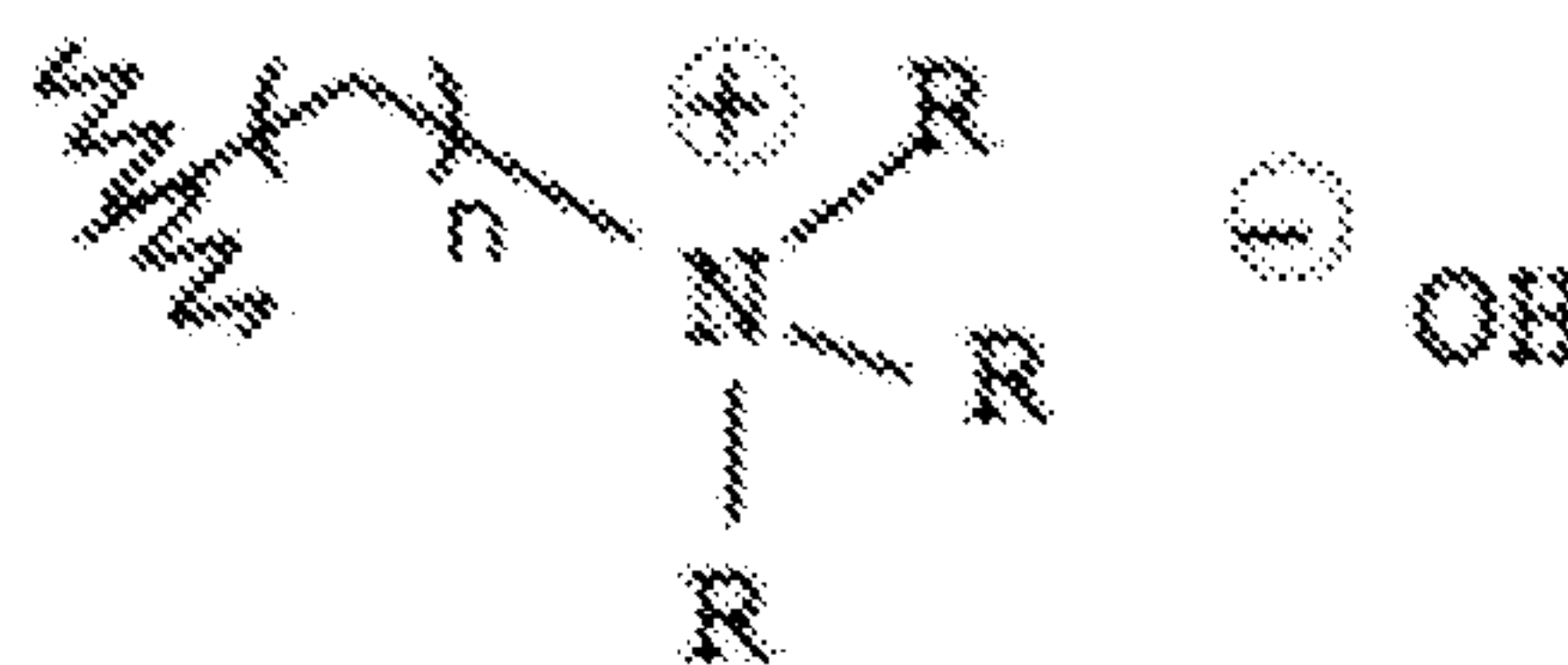
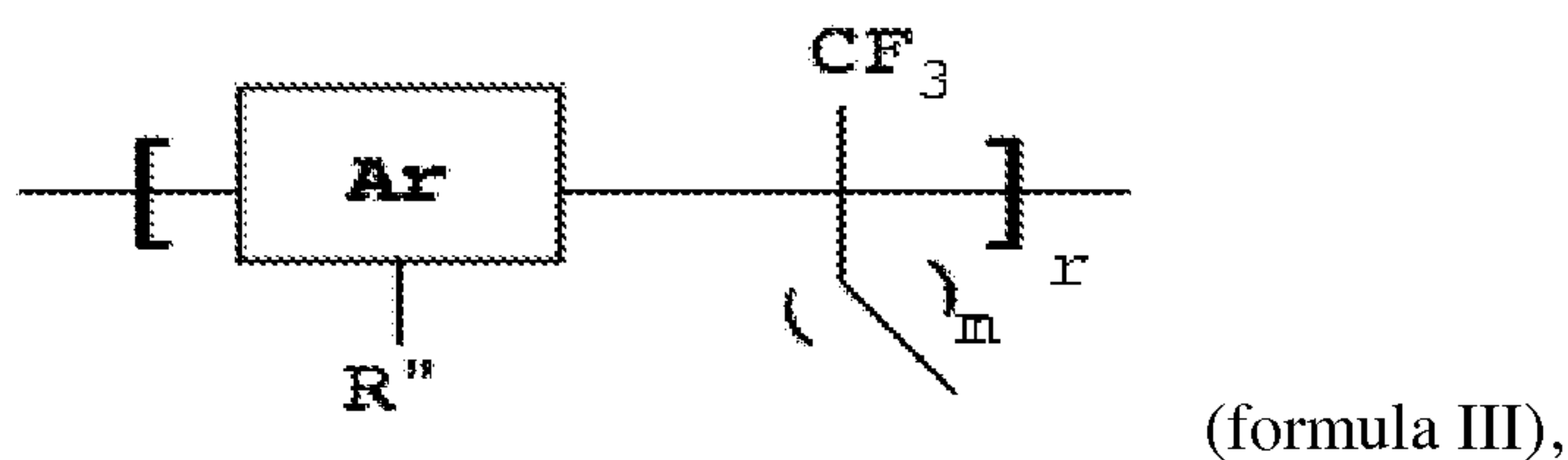
The mechanical properties of AEMs are critically important in fuel cell applications. For each of the PBPA+, PBPA1+, and PBPA2+ polymers, the tensile strength and elongation at the break of the membranes were, respectively, 20–35 MPa and 40–140%, which meet the requirements for building membrane electrode assemblies (MEAs) in AEM fuel cells.

FIG. 5 show stress versus strain curves (panel (a)) for all three polymers. At 50 °C and 50% relative humidity, membranes comprising the polymer with the lowest IEC (PBPA2+) had a mechanical strength (35 MPa) greater than that of a membrane comprising PBPA+ (22 MPa), the polymer with the highest IEC. And compared to Diels–Alder poly(phenylene) AEMs (IEC = 1.7 mequiv/g, 32 MPa maximum strength, 40% maximum strain), membranes comprising the PBPA1+ polymer showed similar tensile strength (IEC = 1.9 mequiv/g, 33 MPa maximum strength, 100% maximum strain) but significantly better elongation at break, likely due to its more flexible backbone structure having a quaternary sp^3 carbon. These mechanical strength data indicate that the polymers of the invention are tough and ductile enough for use as AEM materials in fuel cells.

Panel (b) of FIG. 5 shows the polarization curves of fuel cells containing PBPA1+ at 80 °C. The open-circuit voltage (OCV) was 1.01 V, which is typical in hydrogen-supplied fuel cells. The maximum power density of 155 mW/cm² was obtained at 80 °C and the high-frequency resistance (HFR) of the cell was <0.1 Ωcm^2 . While the membrane conductivity obtained from the HFR is 19.9 S/cm, lower than the value from the *ex situ* measurement due to the nonmembrane resistance contributions of the MEA, the HFR value reported here was much smaller than typical values found in literature reports of AEM fuel cells.

These results clearly demonstrate the superior chemical stability and fuel cell performance of QA poly(biphenyl alkylene)s according to the invention, as compared to other AEM materials.

Polyarylenes other than the poly(biphenyl alkylene)s described above are within the scope of the invention and may be manufactured according to similar methods. For example, methods of the invention may be employed to manufacture a polymer according to formula III

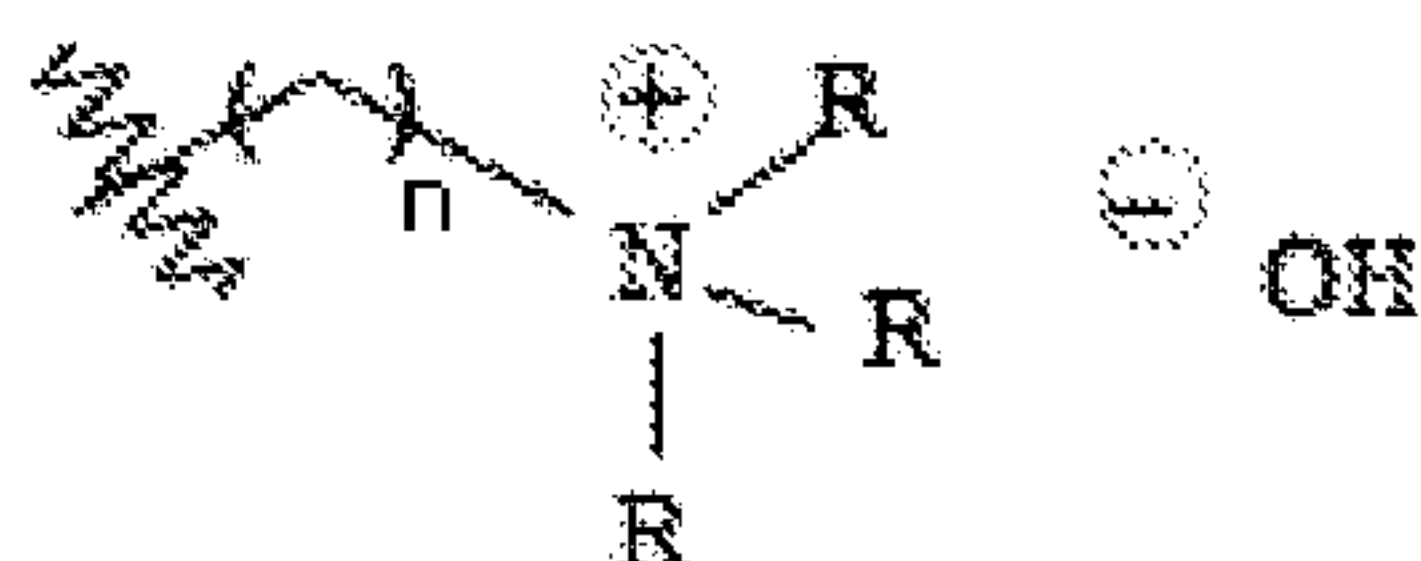


wherein Ar is an aromatic compound, R'' is , r is from 100 to 1,000,000, and m is from 0 to 20.

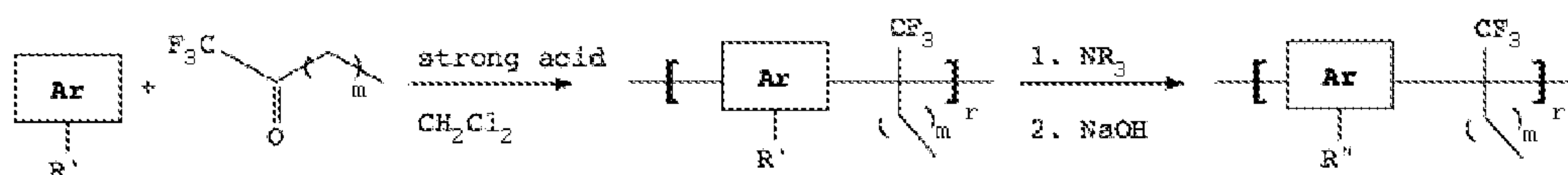
According to some embodiments of the invention, polymers of formula III may be manufactured according to Reaction 2 below, wherein Ar is a polyarylene, R' is



, m is from 0 to 20, r is from 100 to 1,000,000, R is an aryl group,

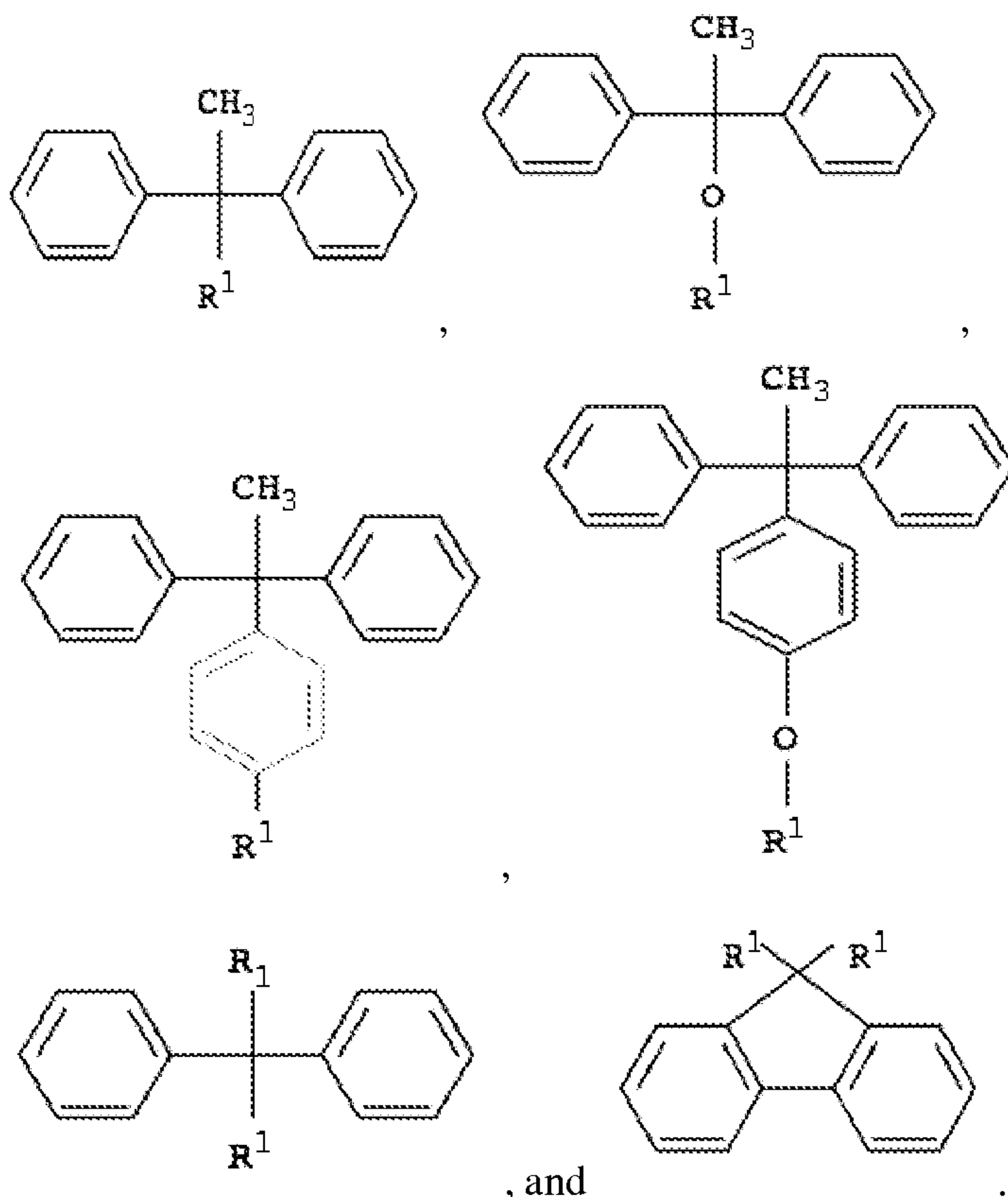


and R'' is .

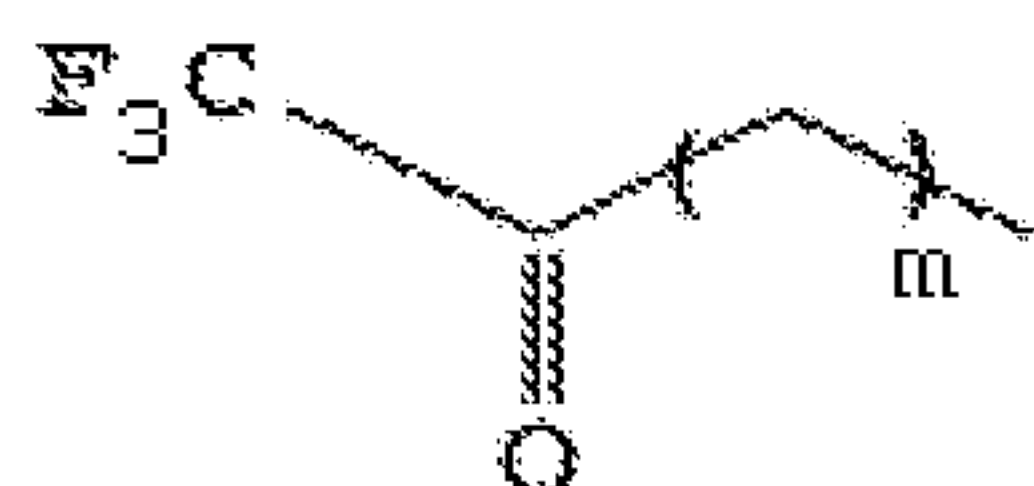


(Reaction 2)

According to some embodiments of the invention, the aromatic compound is selected from a group consisting of:



Other aromatic compounds may be employed, of course, as will be recognized by one skilled in the art and are within the scope of the invention. Similarly, in some embodiments,



is methyl trifluoromethyl ketone. Other trifluoroalkyl ketones will be apparent to one skilled in the art and are within the scope of the invention.

Finally, although the embodiments above include brominated aromatic compounds or trifluoroalkyl ketones, other halogens may be employed. For example, 7-chloro-1,1,1-trifluoroheptan-2-one could be employed to prepare a chloroalkylated precursor polymer, from which polymers according to the invention are prepared through nucleophilic substitution. In such embodiments, groups other than ammonium groups (*e.g.*, alkyloxy, sulfonate, carboxylate, phosphonate) may be included in the resulting polymer.

As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” when used in this specification, specify the presence of stated features, integers, steps, operations,

1 elements, and/or components, but do not preclude the presence or addition of one or
2 more other features, integers, steps, operations, elements, components, and/or groups
3 thereof.

4 This written description uses examples to disclose the invention, including the
5 best mode, and also to enable any person skilled in the art to practice the invention,
6 including making and using any devices or systems and performing any related or
7 incorporated methods. The patentable scope of the invention is defined by the claims,
8 and may include other examples that occur to those skilled in the art. Such other
9 examples are intended to be within the scope of the claims if they have structural
10 elements that do not differ from the literal language of the claims, or if they include
11 equivalent structural elements with insubstantial differences from the literal language
12 of the claims.

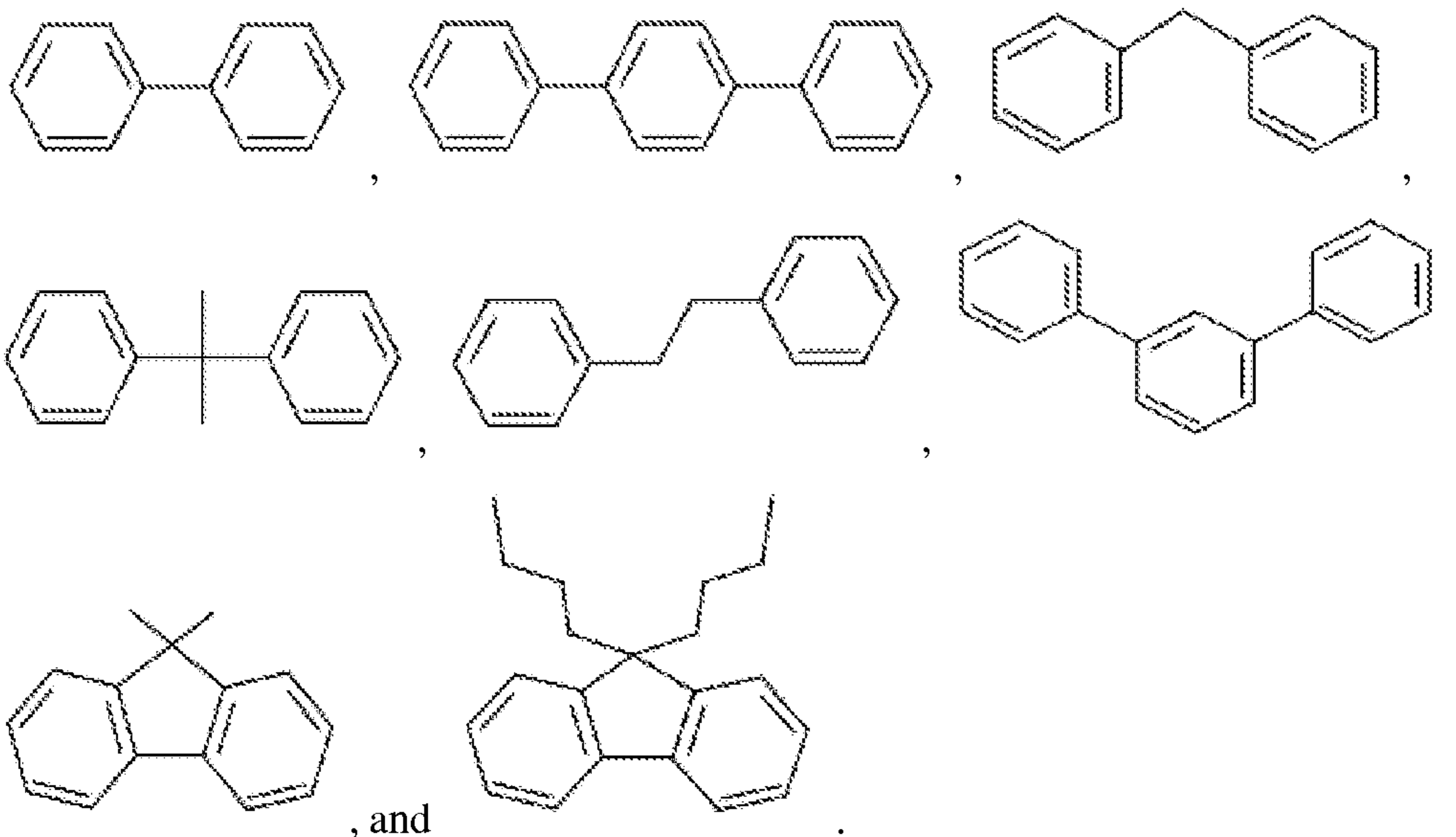
CLAIMS

What is claimed is:

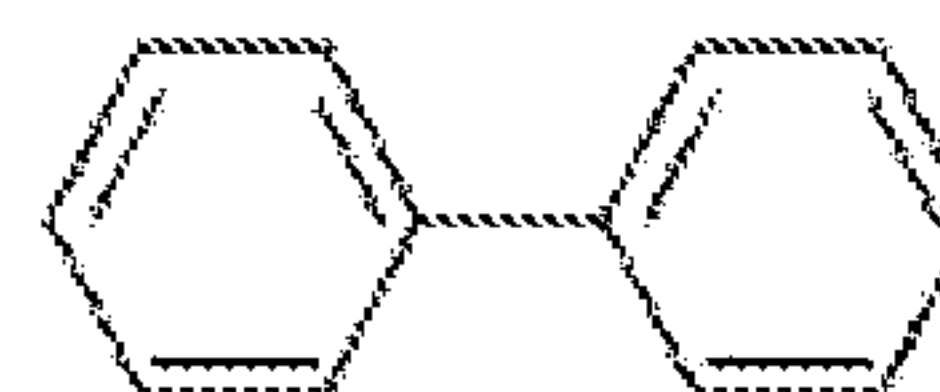
1. A method of forming a polyarylene, the method comprising:
 - reacting an aromatic compound and a trifluoroalkyl ketone in the presence of a strong acid to form a bromoalkylated precursor polymer; and
 - reacting the bromoalkylated precursor polymer with a trialkylamine and sodium hydroxide to form a polyarylene having a main chain free of ether linkages.

2. The method of claim 1, wherein the trifluoroalkyl ketone includes at least one trifluoroalkyl ketone selected from a group consisting of: 7-bromo-1,1,1-trifluoroheptan-2-one and methyl trifluoromethyl ketone.

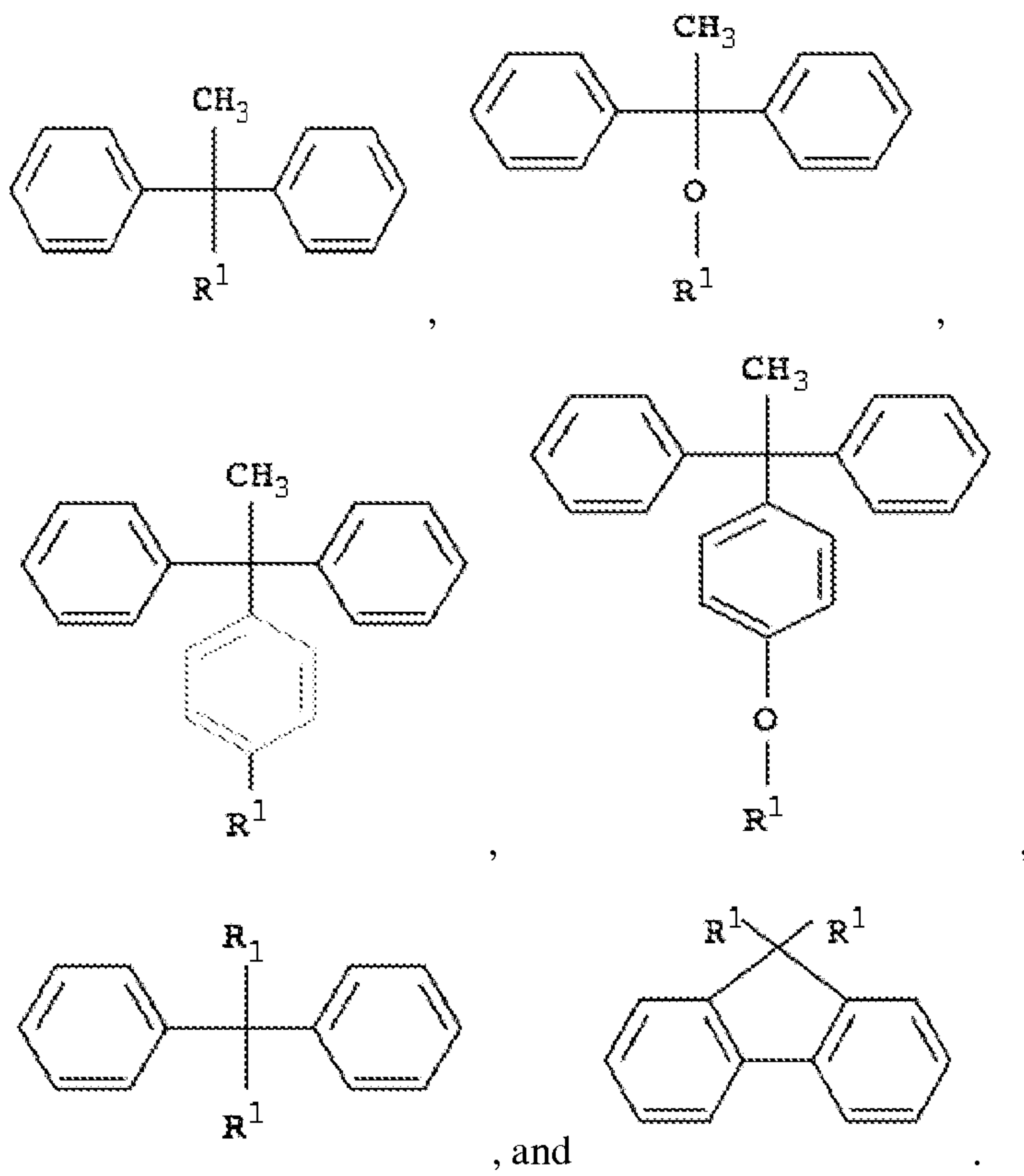
3. The method of claim 1, wherein the aromatic compound is selected from a group consisting of:



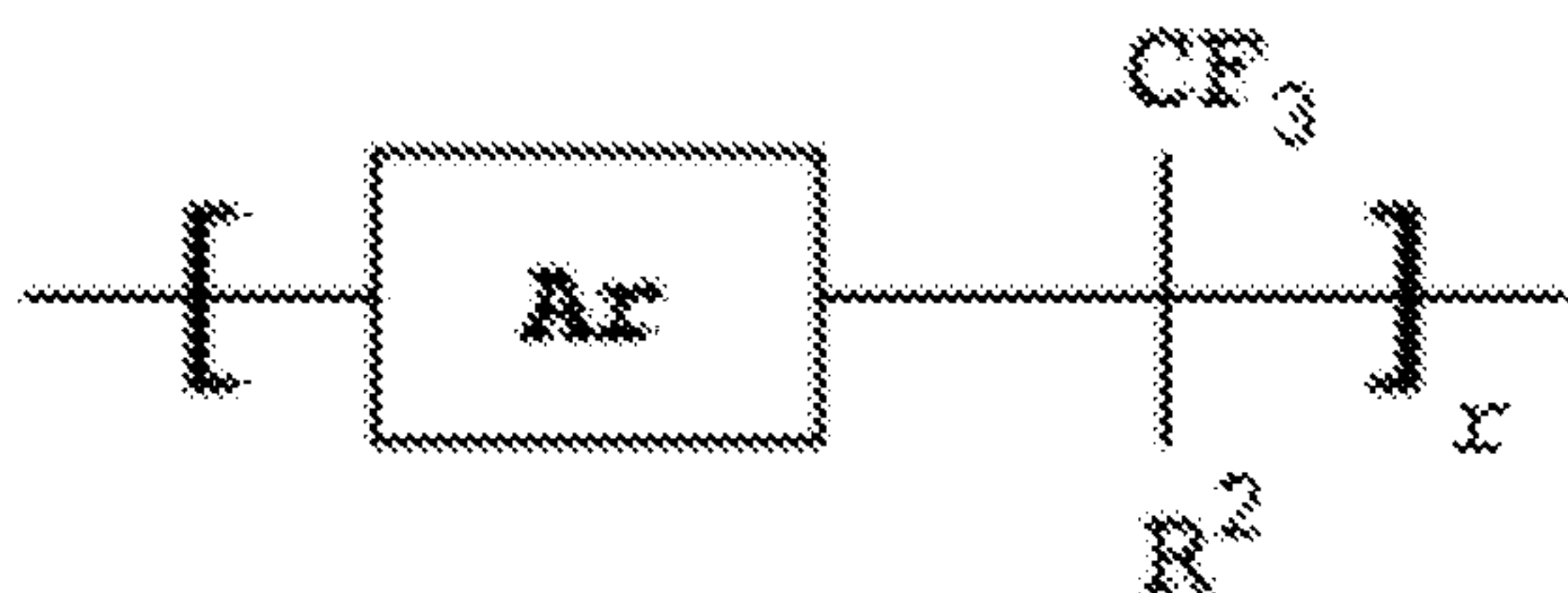
4. The method of claim 3, wherein the aromatic compound is



5. The method of claim 1, wherein the aromatic compound is selected from a group consisting of:

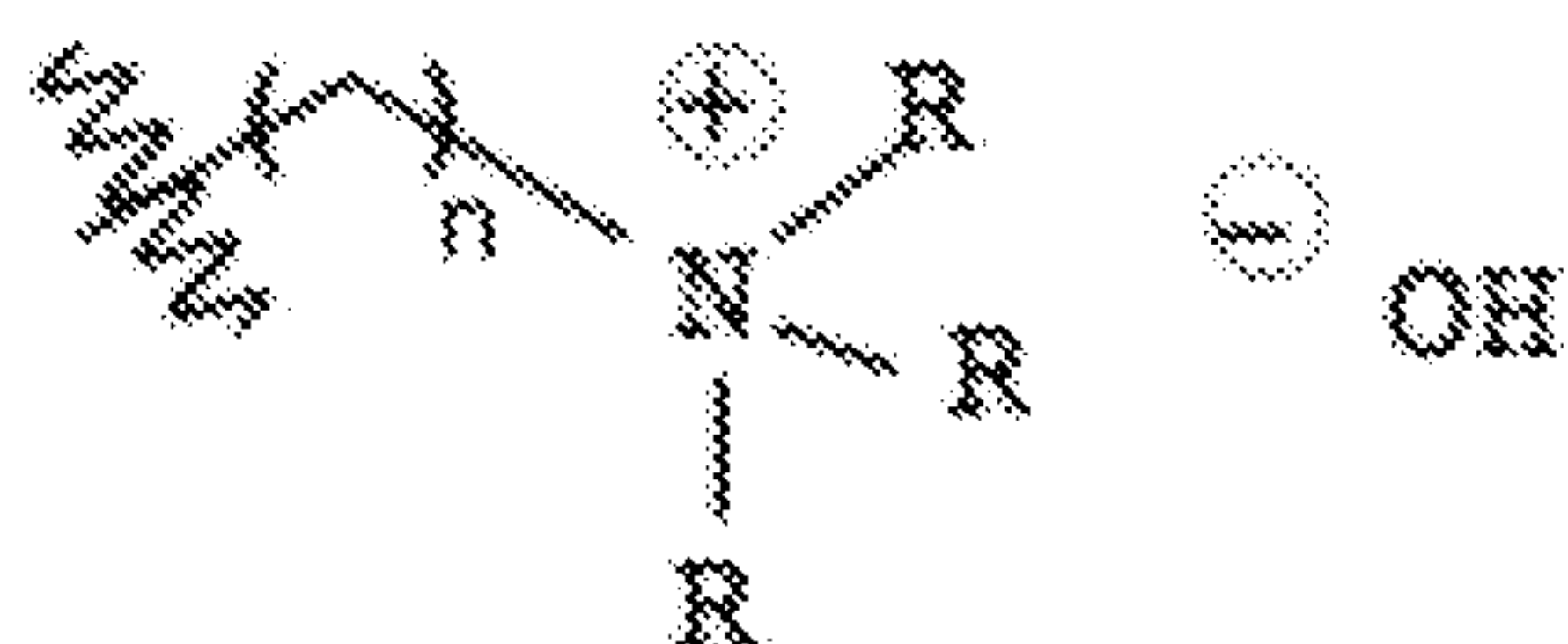


6. A polymer of formula I prepared according to the method of claim 1

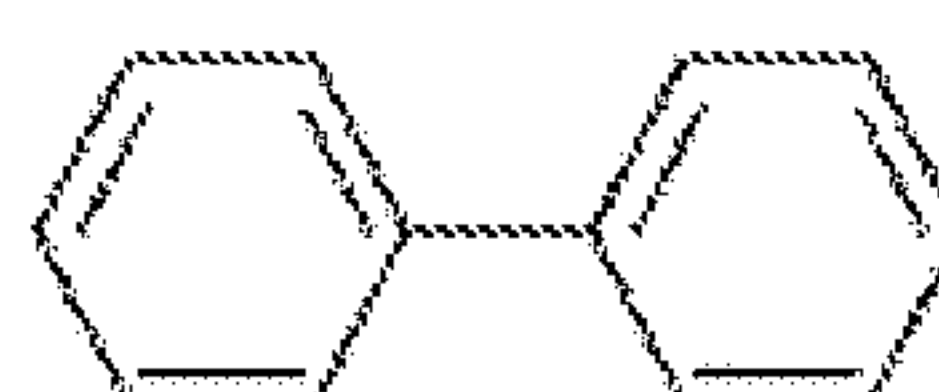


(formula I),

wherein Ar is an aromatic compound, x is from 100 to 1,000,000, R^2 is

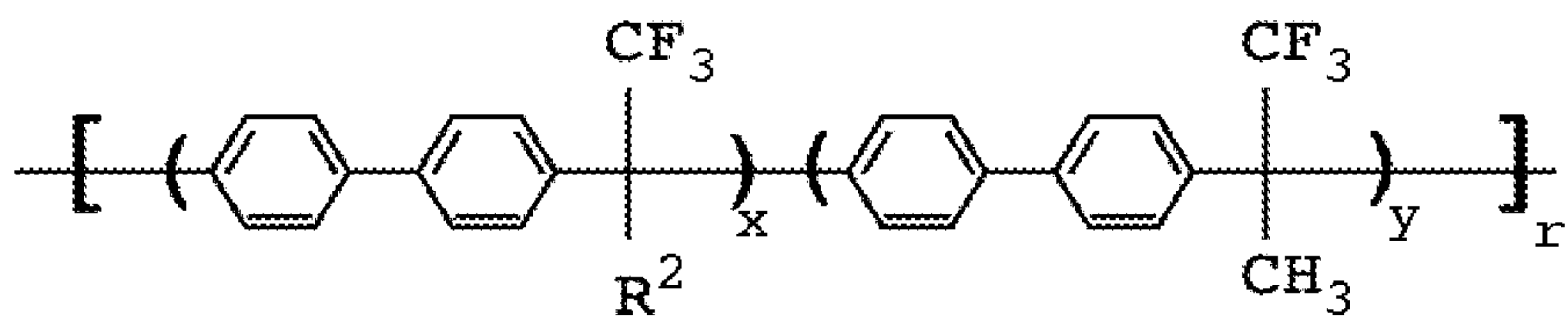


, R is an alkyl group, and n is from 1 to 20.



7. The polymer of claim 6, wherein Ar is

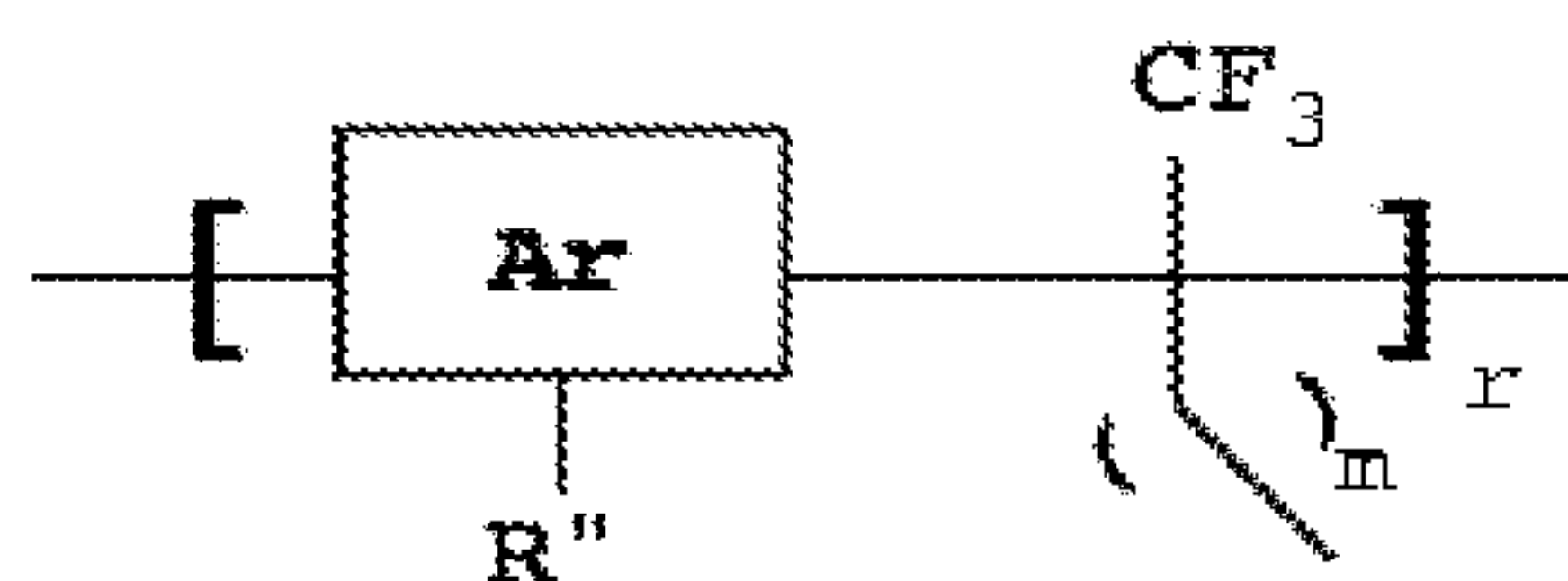
8. The polymer of claim 7 having formula IA



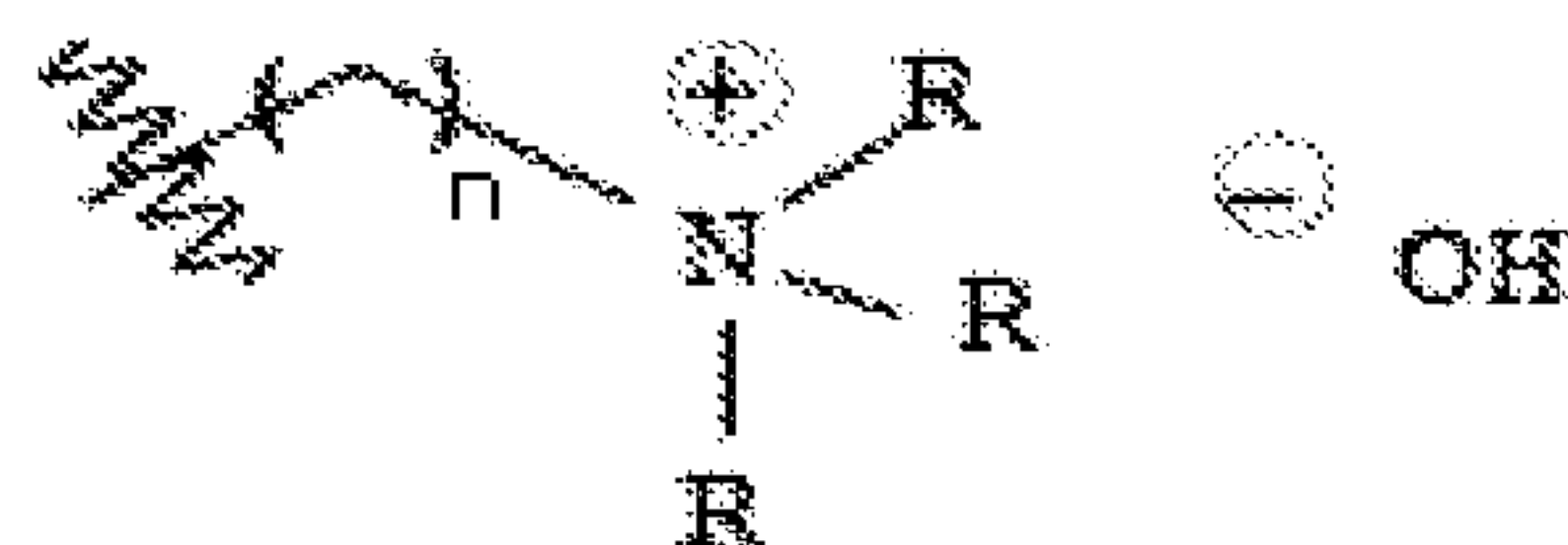
wherein $x + y = 1$.

9. The polymer of claim 8, wherein x is 1 and y is 0, or x is 0.65 and y is 0.35, or x is 0.44 and y is 0.56.

10. A polymer of formula III prepared according to the method of claim 1



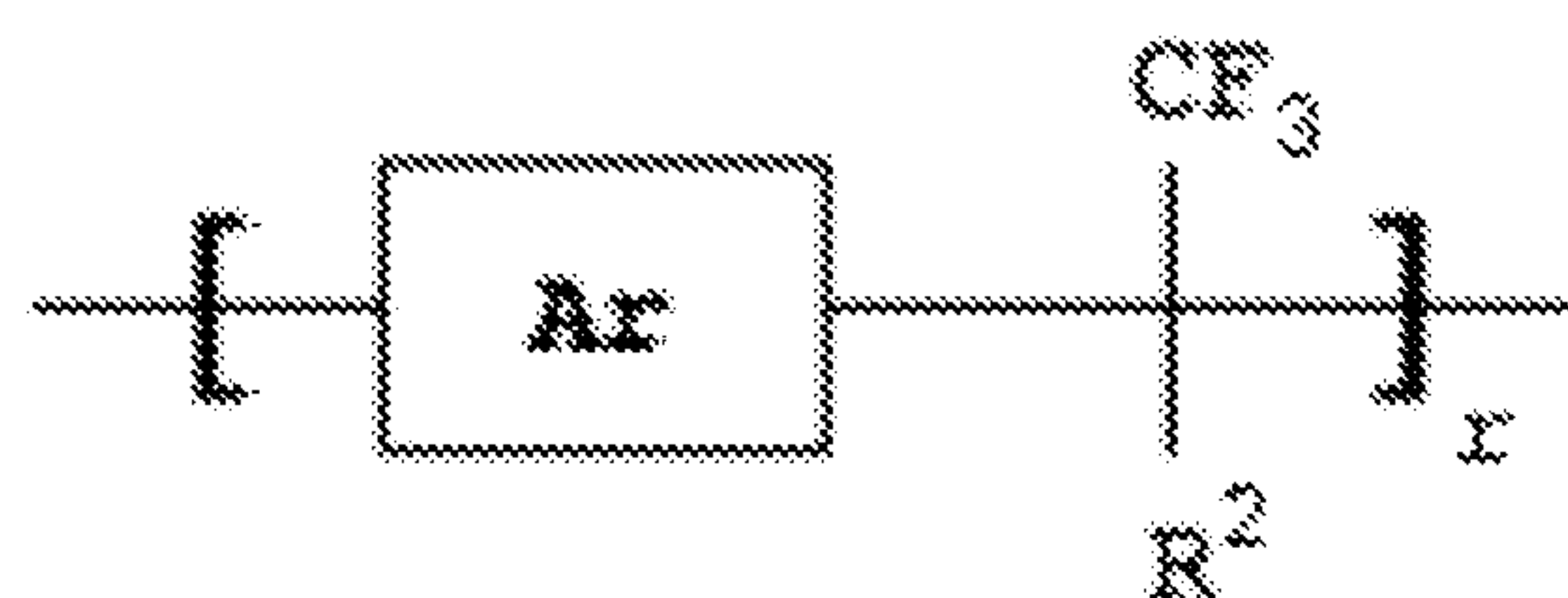
(formula III),



wherein Ar is an aromatic compound, R" is

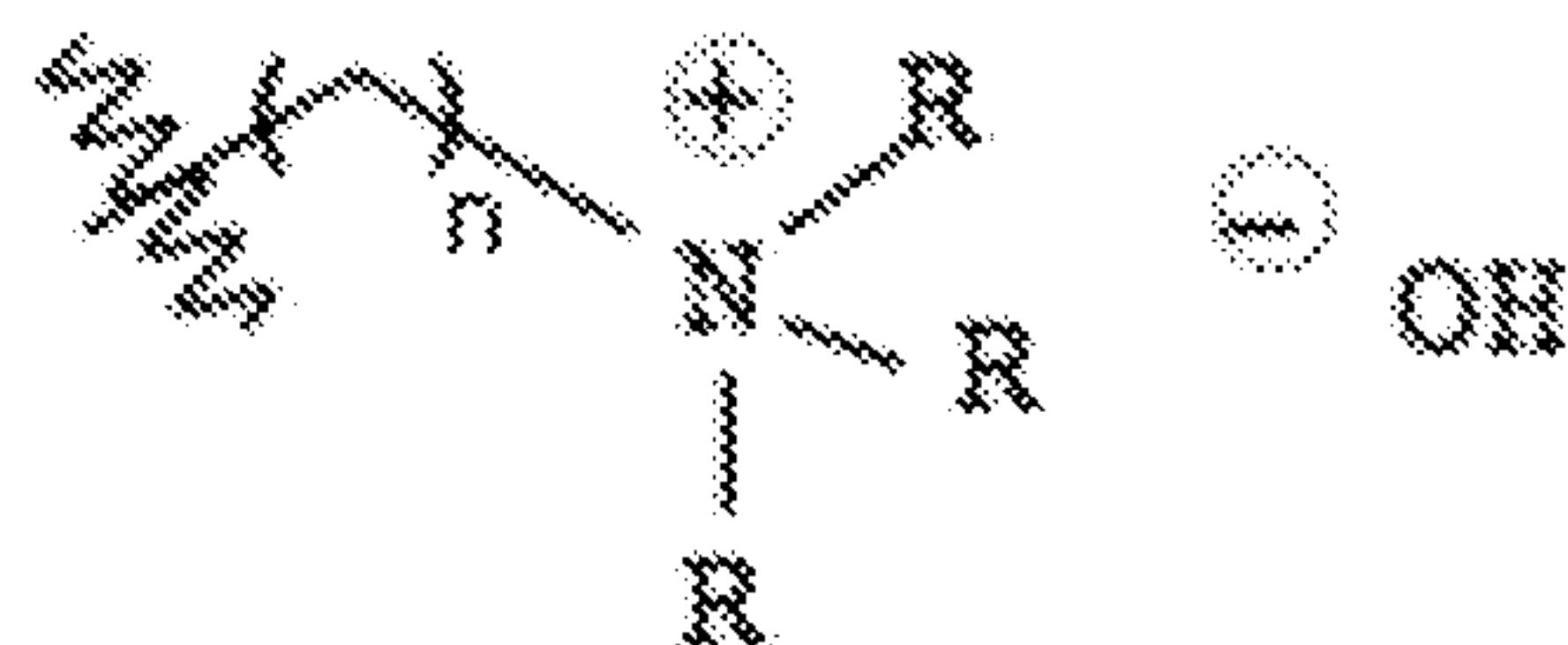
is from 100 to 1,000,000, and m is from 0 to 20.

1 11. A polymer according to formula I



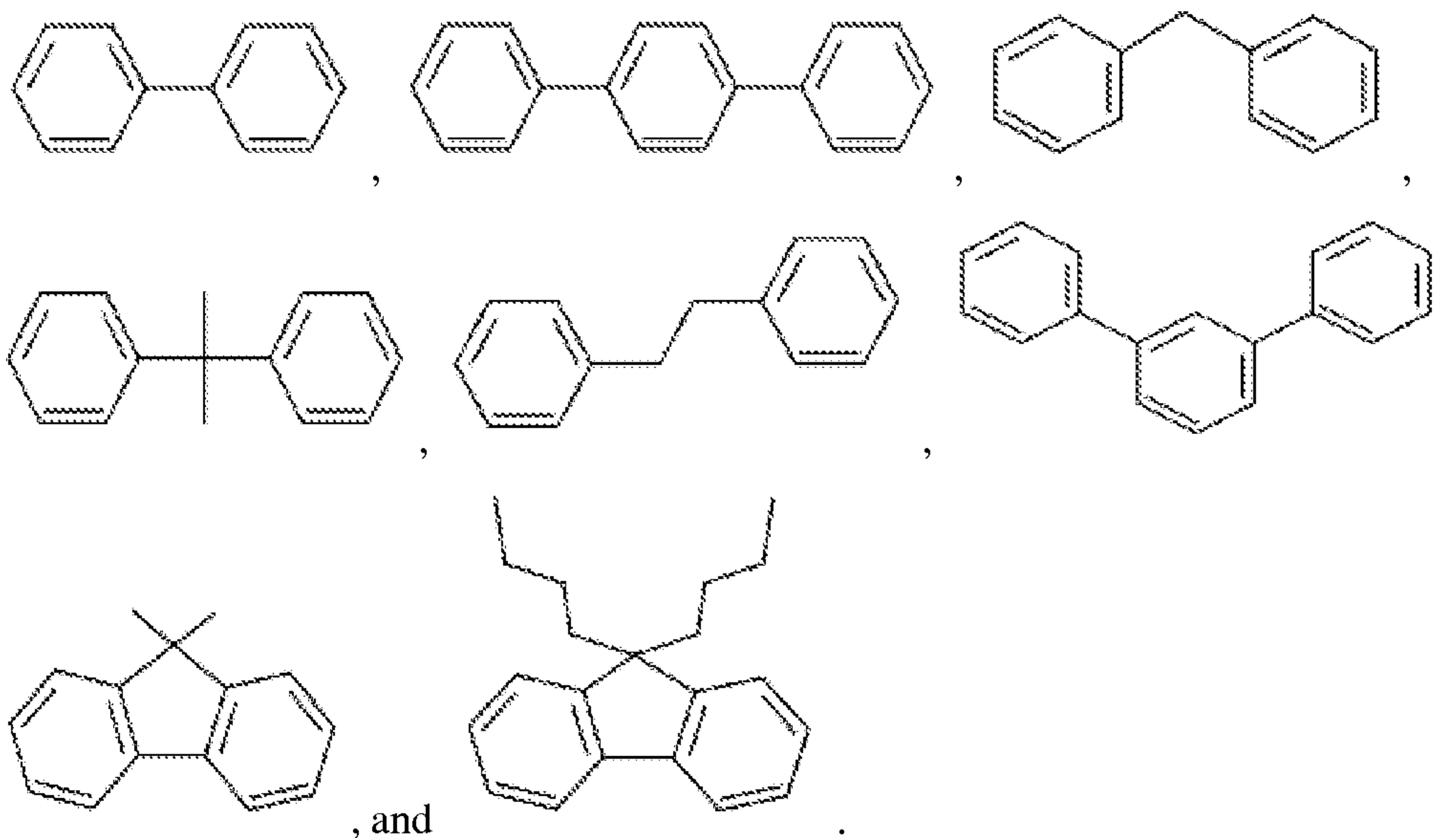
(formula I),

2 wherein Ar is an aromatic compound, r is from 100 to 1,000,000, R² is



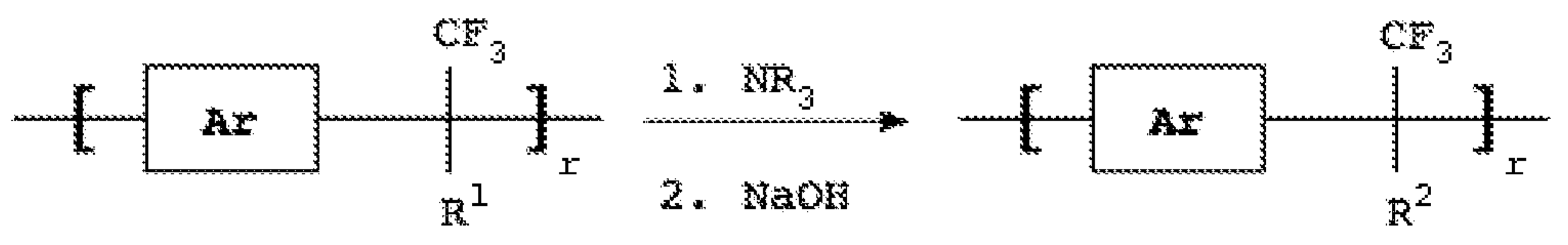
3 , R is an alkyl group, and n is from 1 to 20.

4
5
6 12. The polymer of claim 11, wherein the aromatic compound is selected from a
7 group consisting of:



13. The polymer of claim 11, prepared from a bromoalkylated precursor polymer of formula II according to the reaction:

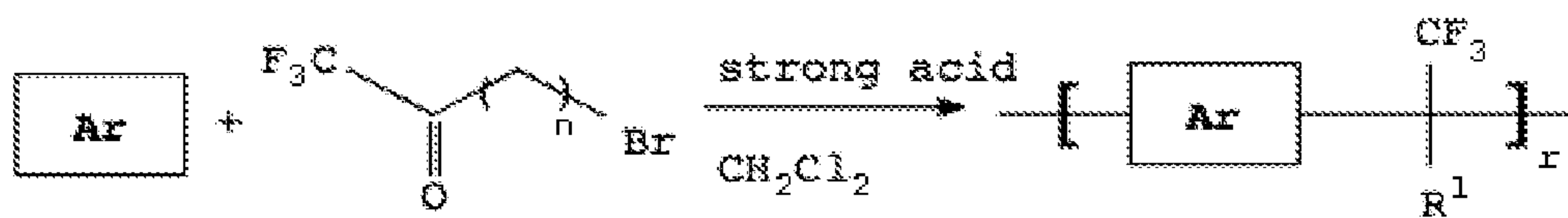
(formula II)



wherein R^1 is

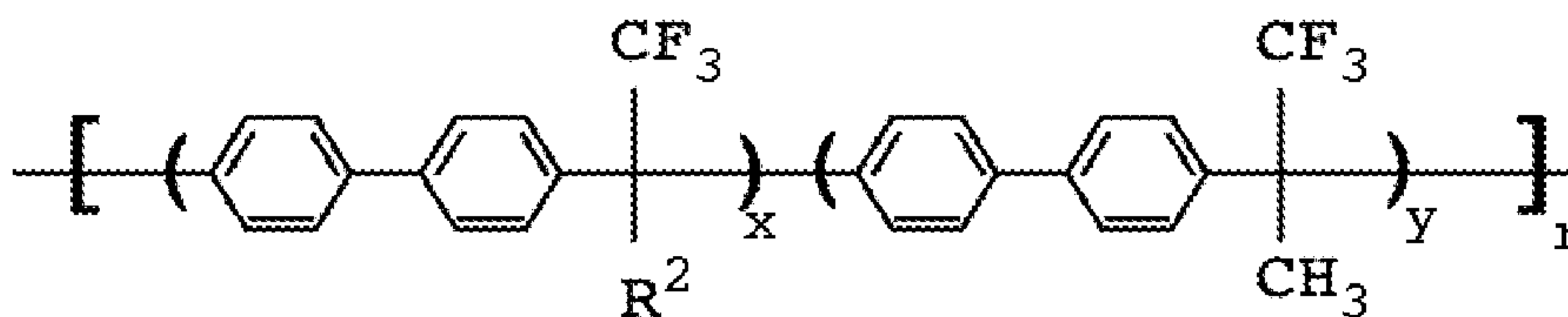
14. The polymer of claim 11, wherein the bromoalkylated precursor polymer of formula II is prepared according to the reaction:

(formula II)



15. The polymer of claim 14, wherein the strong acid is trifluoromethanesulfonic acid.

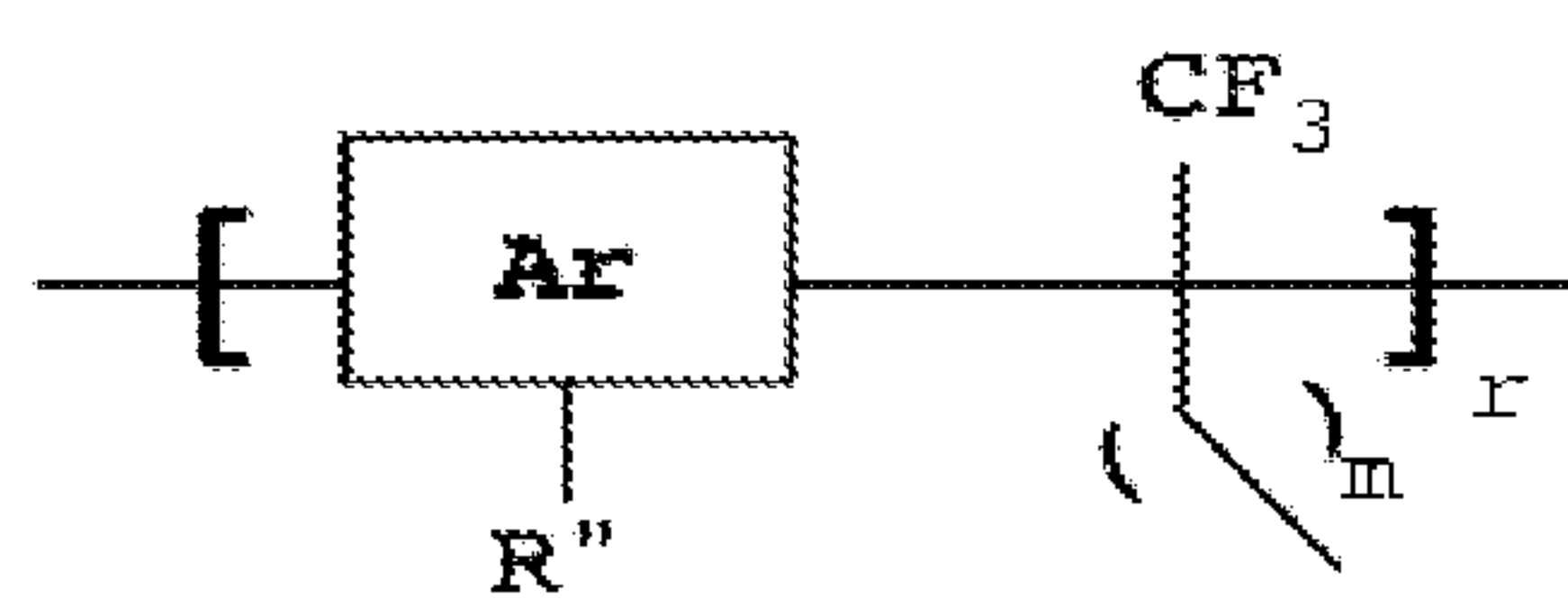
16. The polymer of claim 11 having formula IA



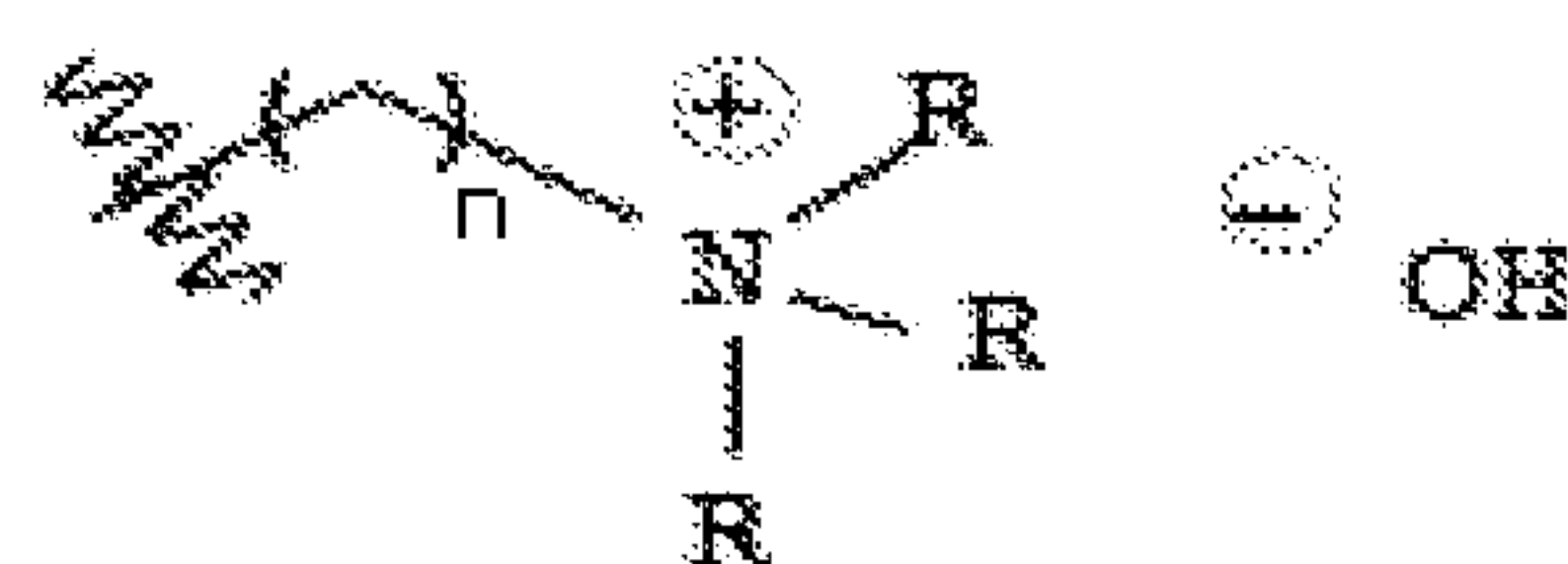
wherein $x + y = 1$.

17. The polymer of claim 16, wherein x is 1 and y is 0, or x is 0.65 and y is 0.35, or x is 0.44 and y is 0.56.

1 18. A polymer according to formula III



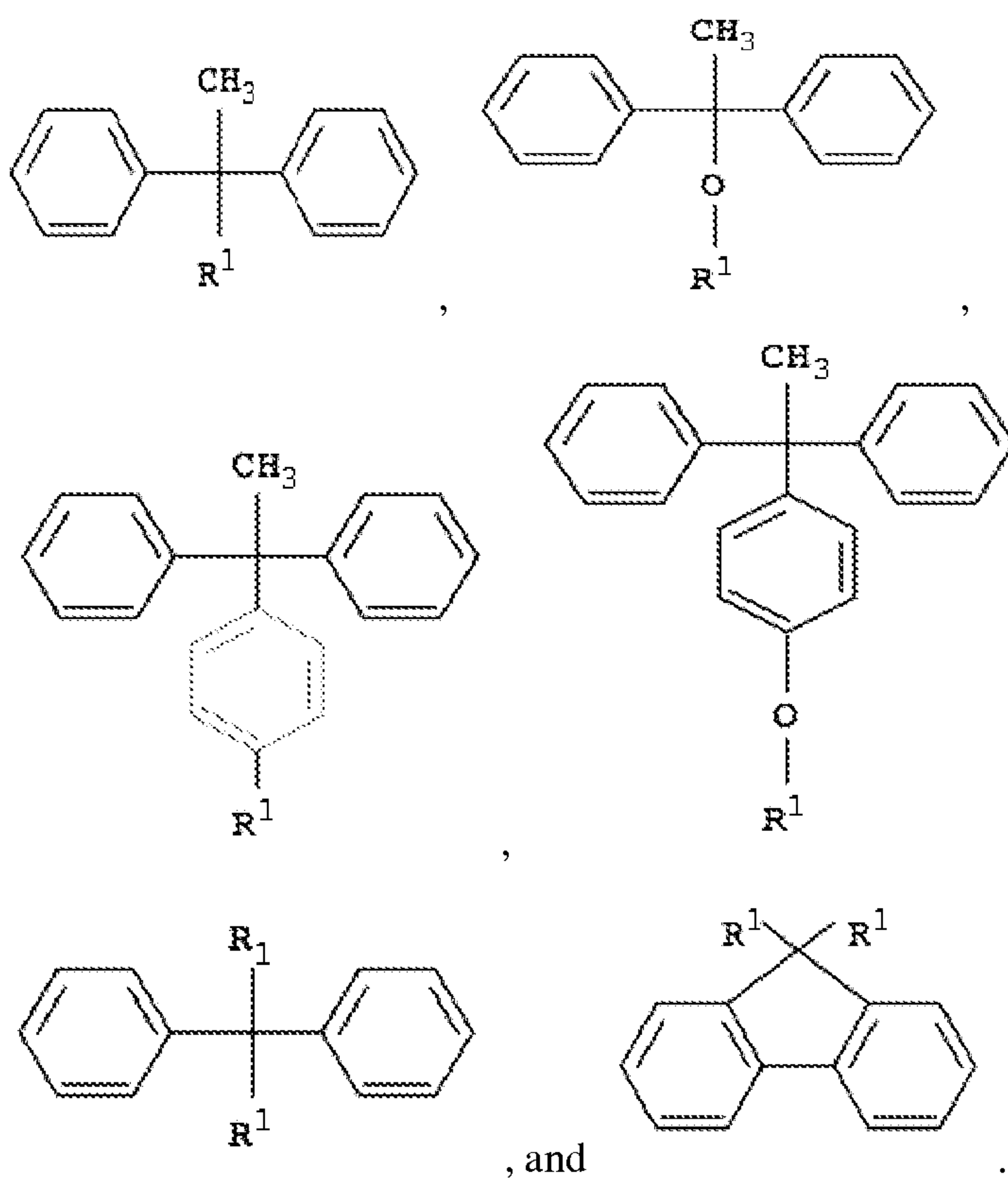
(formula III),



3 wherein Ar is an aromatic compound, R" is

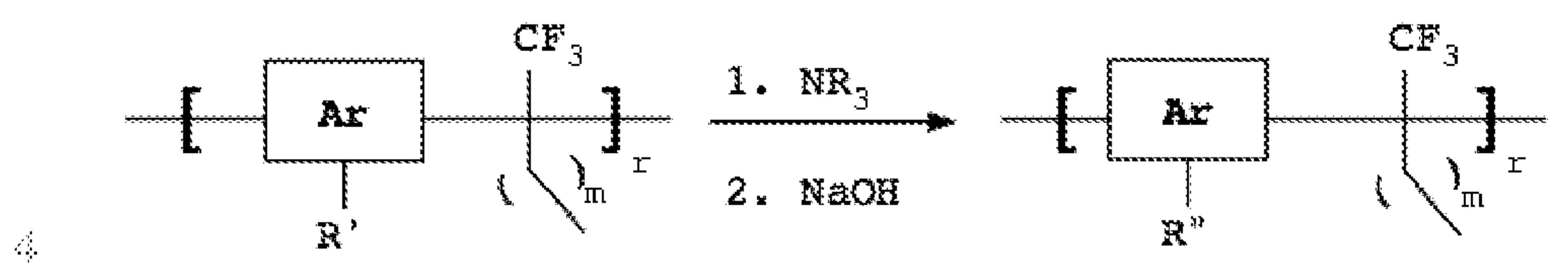
4 is from 100 to 1,000,000, and m is from 0 to 20.

6 19. The polymer of claim 18, wherein the aromatic compound is selected from a
7 group consisting of:



20. The polymer of claim 18, prepared from a bromoalkylated precursor polymer of formula IV according to the reaction:

(formula IV)



wherein R' is $\text{---} \text{C} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{Br}$, n is from 1 to 20, and R is an alkyl group.

FIG. 1

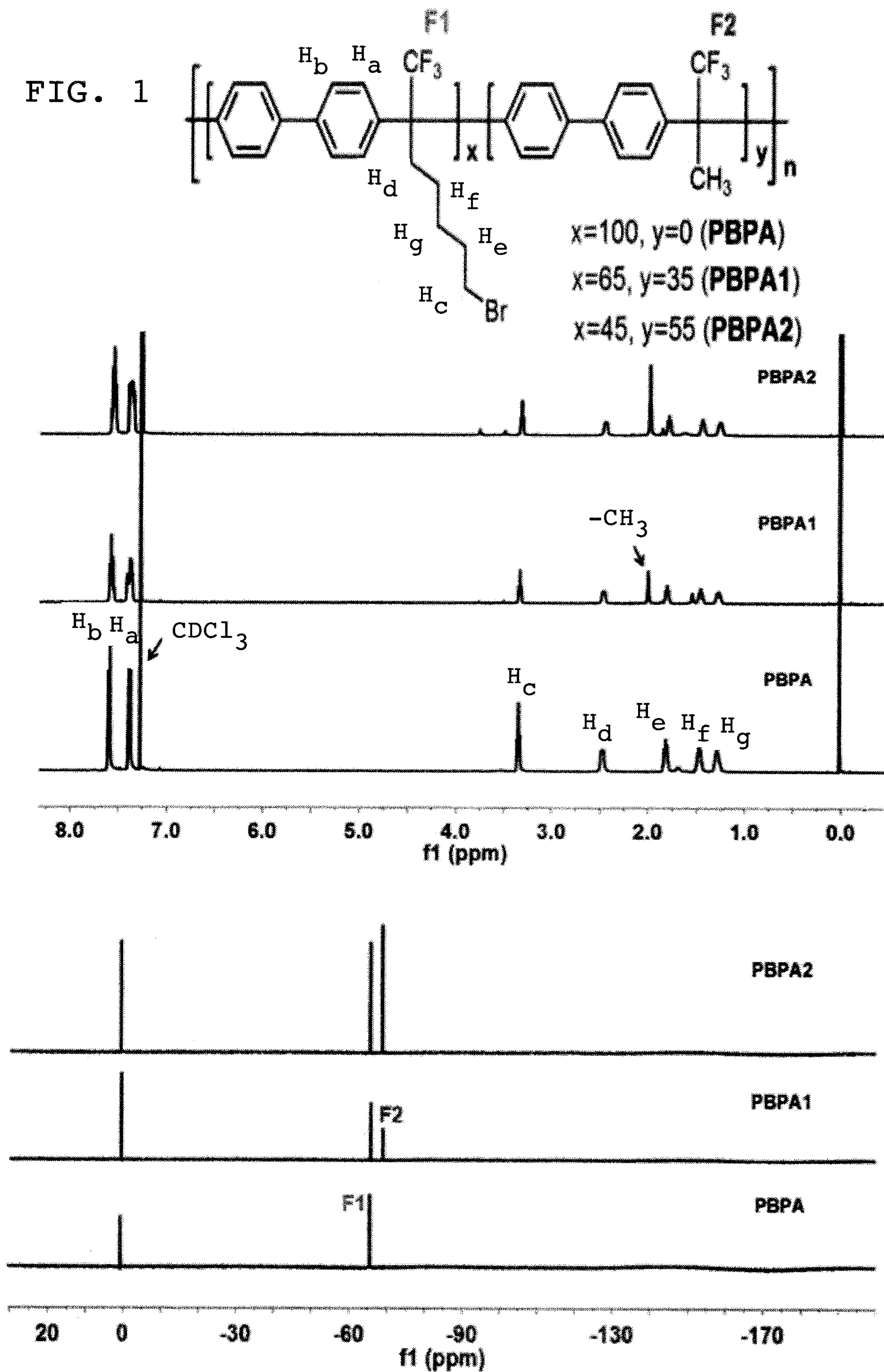


FIG. 2

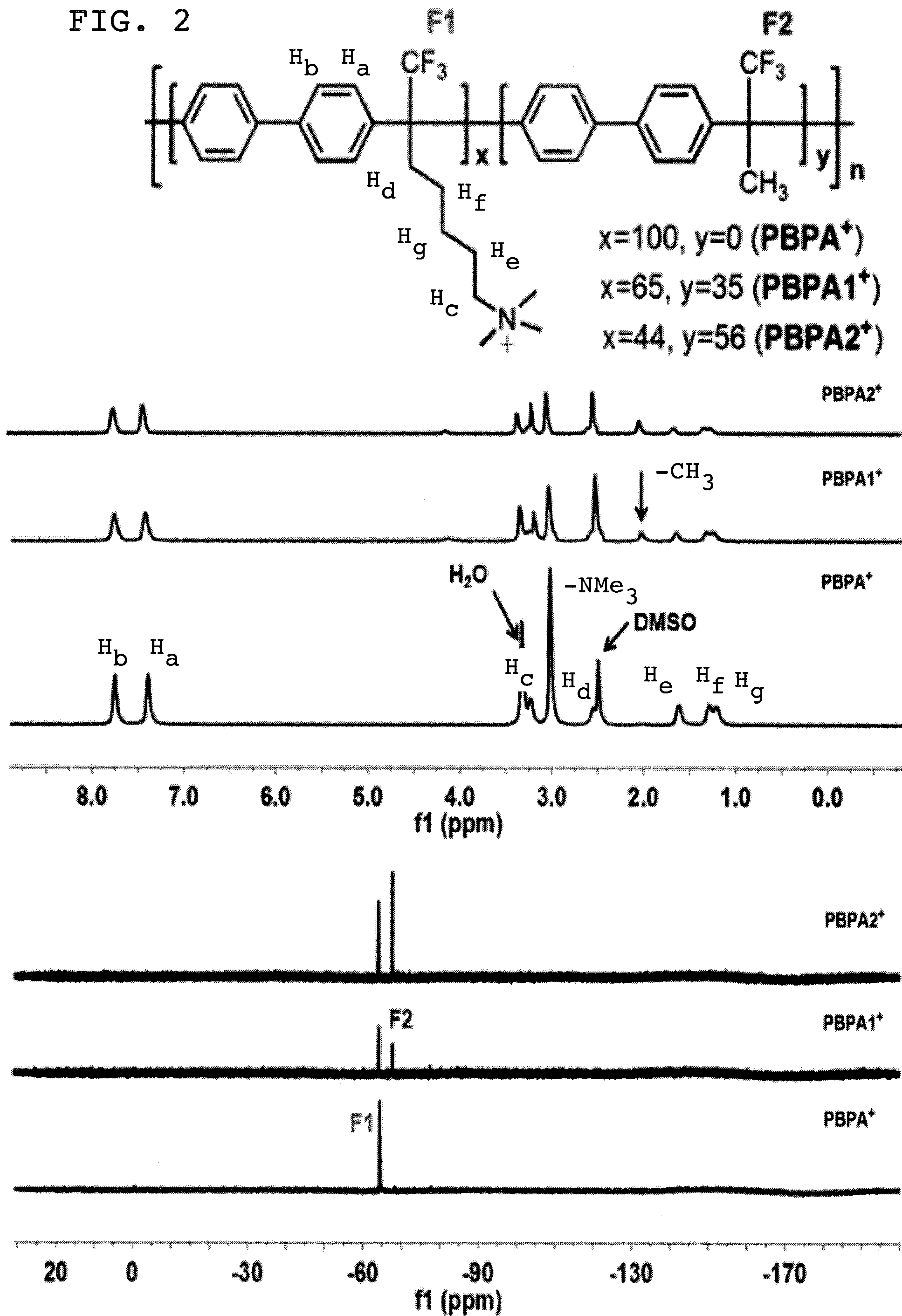


FIG. 3

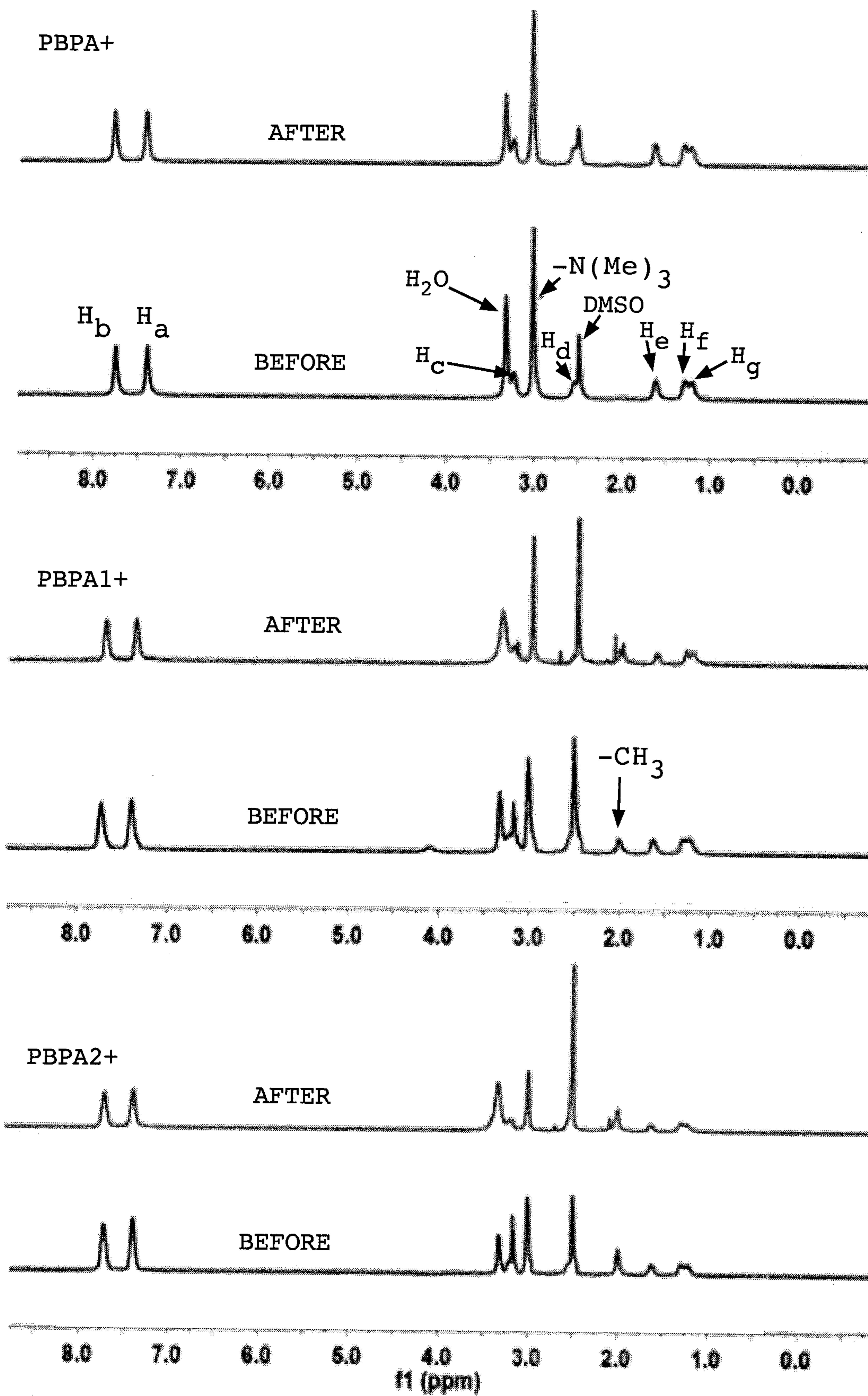


FIG. 4

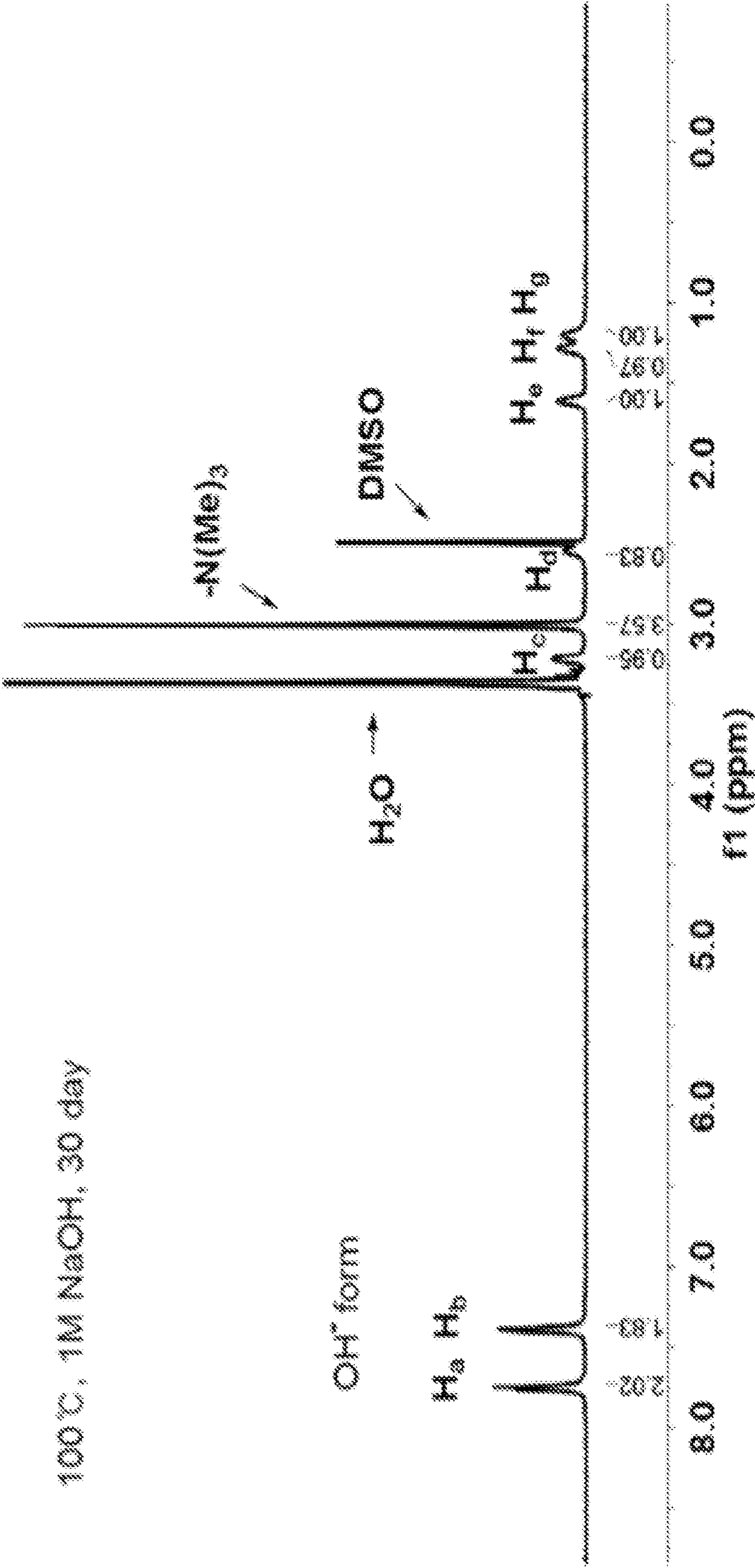


FIG. 5

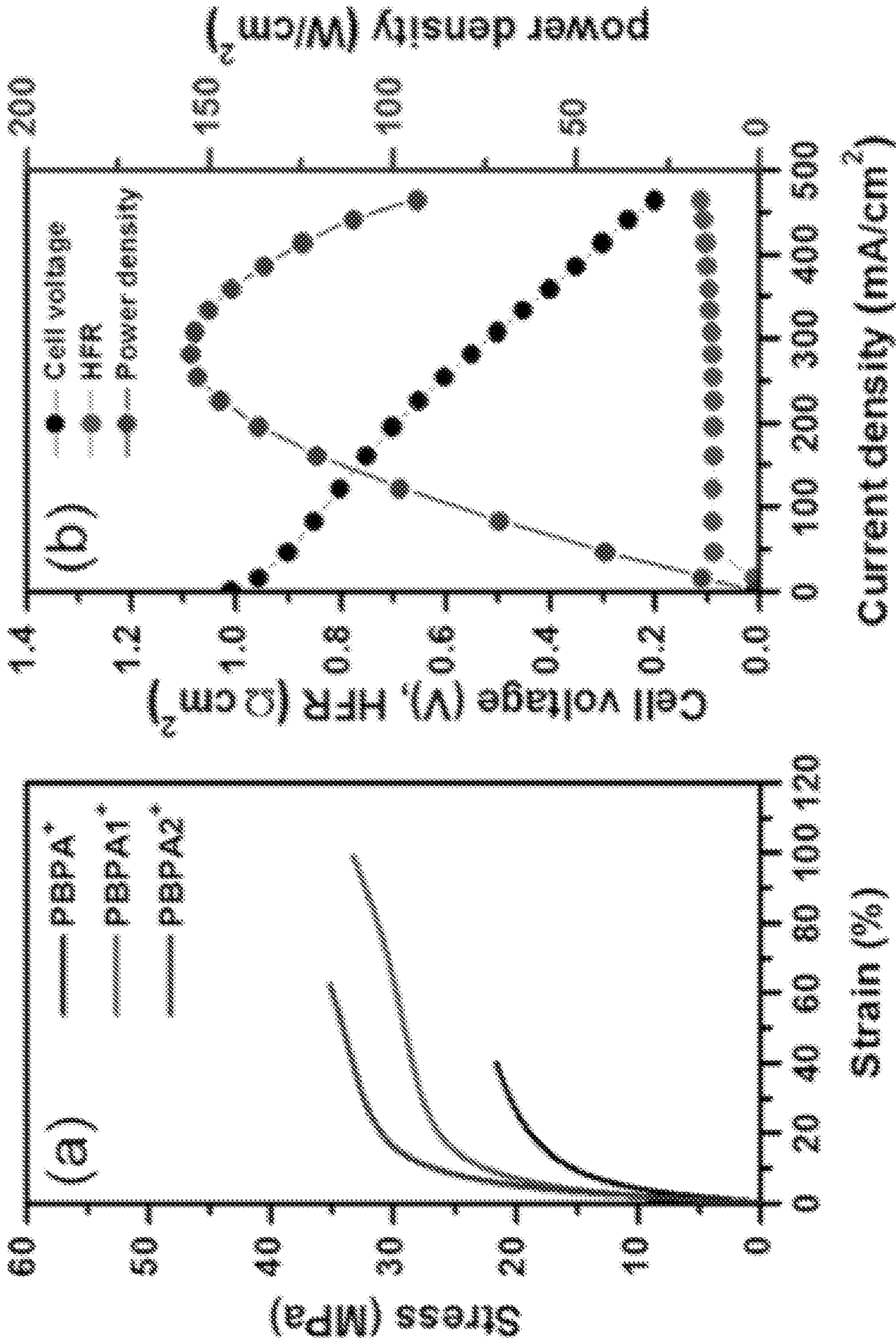


FIG. 2

