

1/93

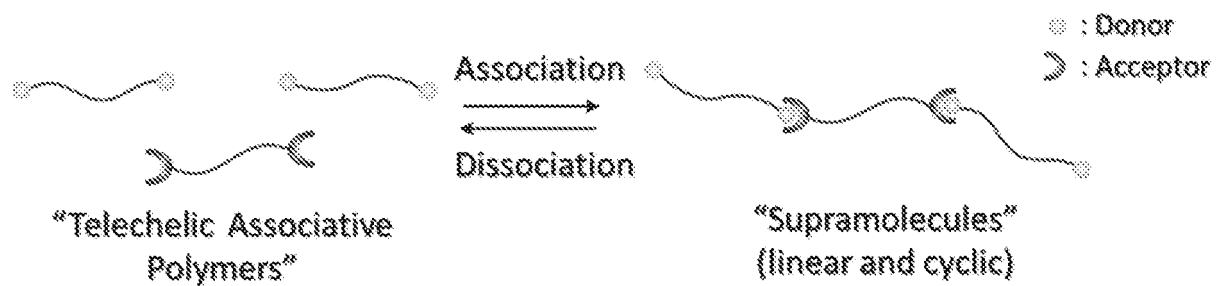


FIG. 1A

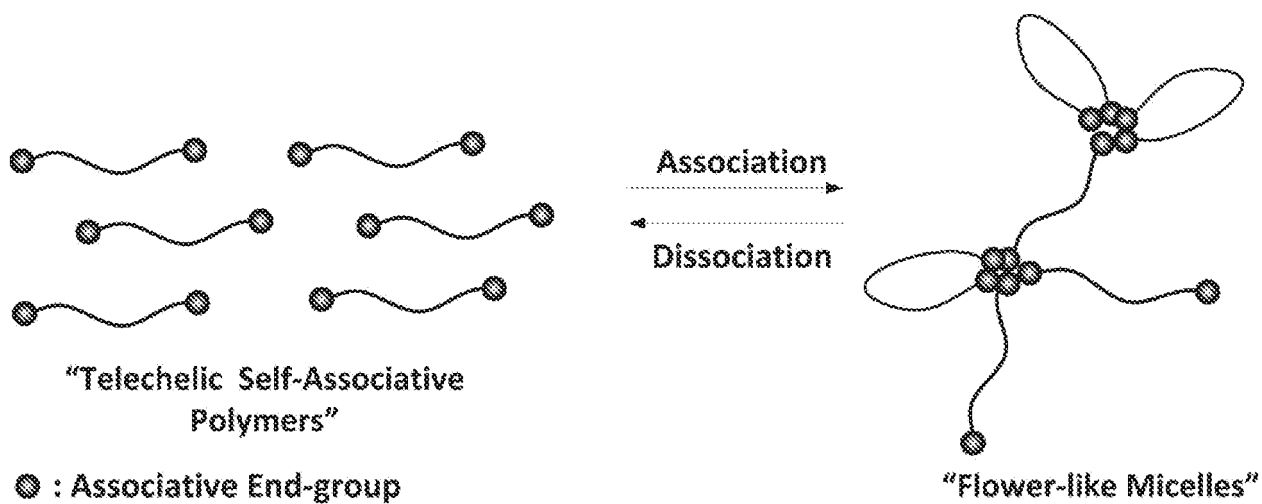


FIG. 1B

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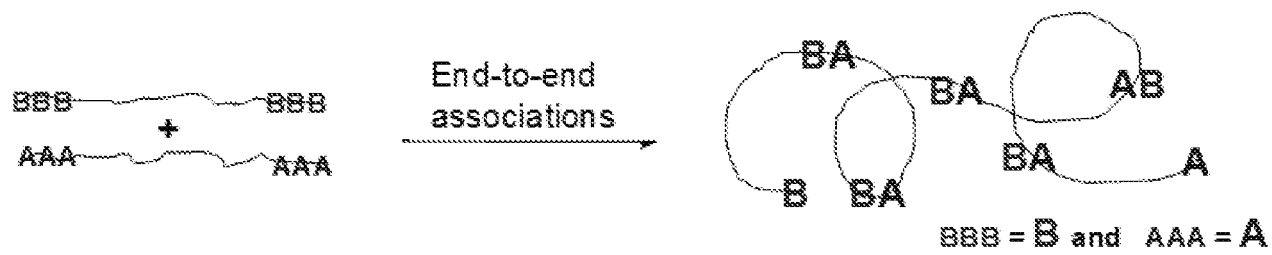
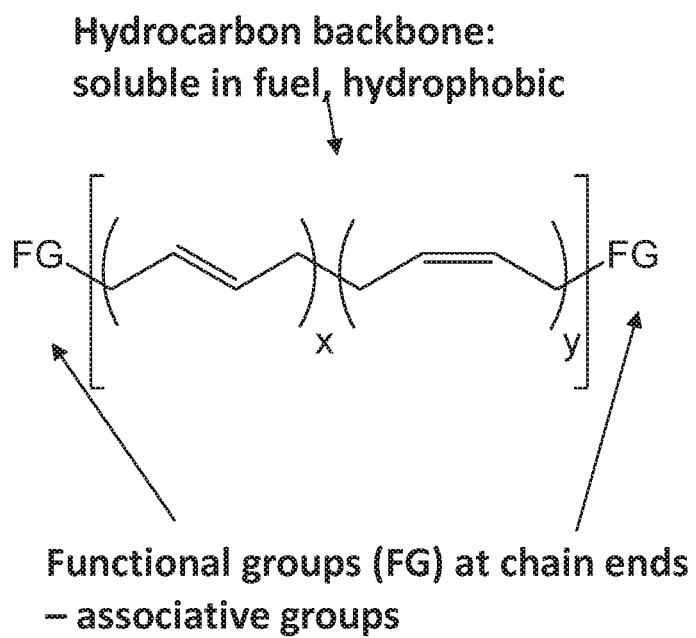


FIG. 2A

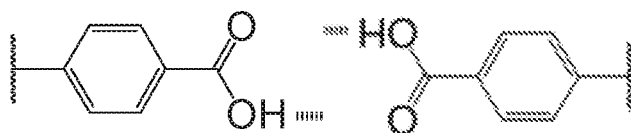


FIG. 2B

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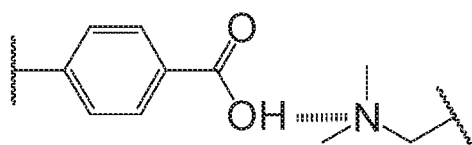
**FIG. 3**

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Examples of Suitable Associative Functional Groups

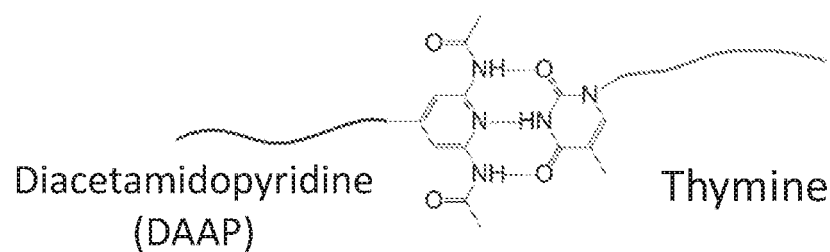
Carboxylic acid

Carboxylic acid

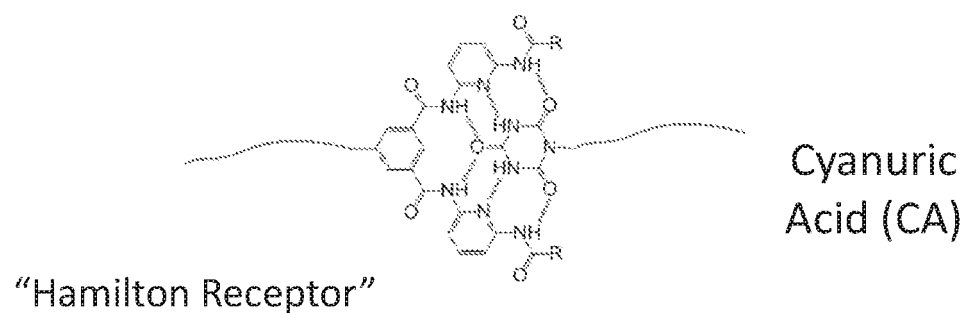


Carboxylic acid

Tertiary amine

Diacetamidopyridine
(DAAP)

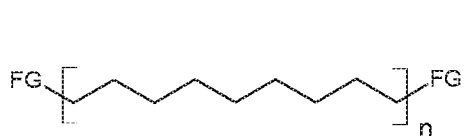
Thymine



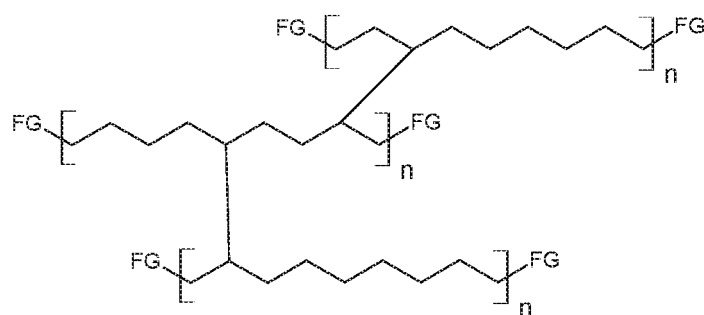
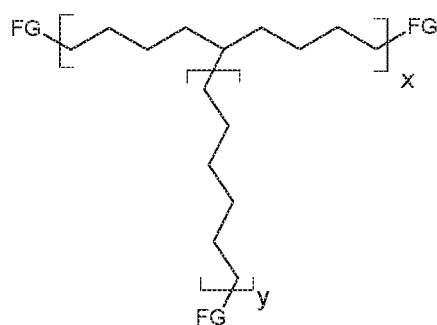
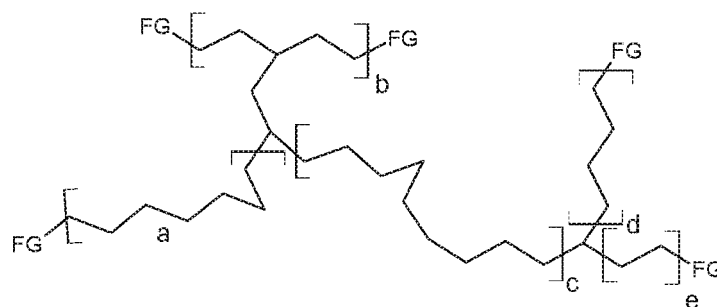
"Hamilton Receptor"

Cyanuric
Acid (CA)**FIG. 4****Exemplary Architectures**

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Linear, difunctional

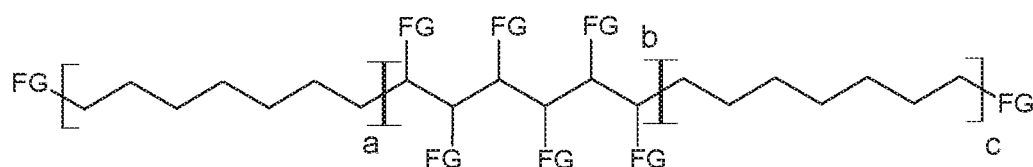
Partially cross-linked
variants, functional at
the chain endsBranched, trifunctional
(tetra, penta, etc.. possible)

Hyperbranched, functional at the chain ends

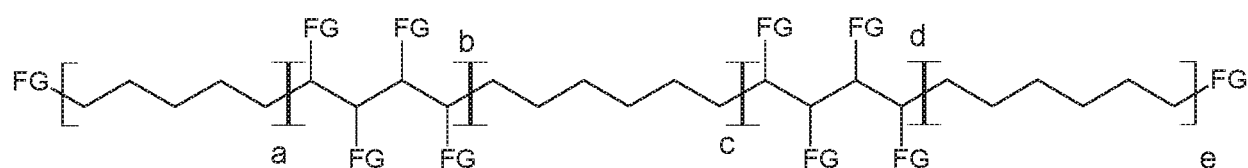
where

represents a generic
polymer backbone
soluble in fuel**FIG. 5**

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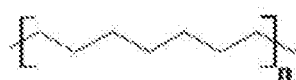
Exemplary Block Architectures

Associative groups at the ends and clustered in the middle



Associative groups at the ends and several clusters along the chain length

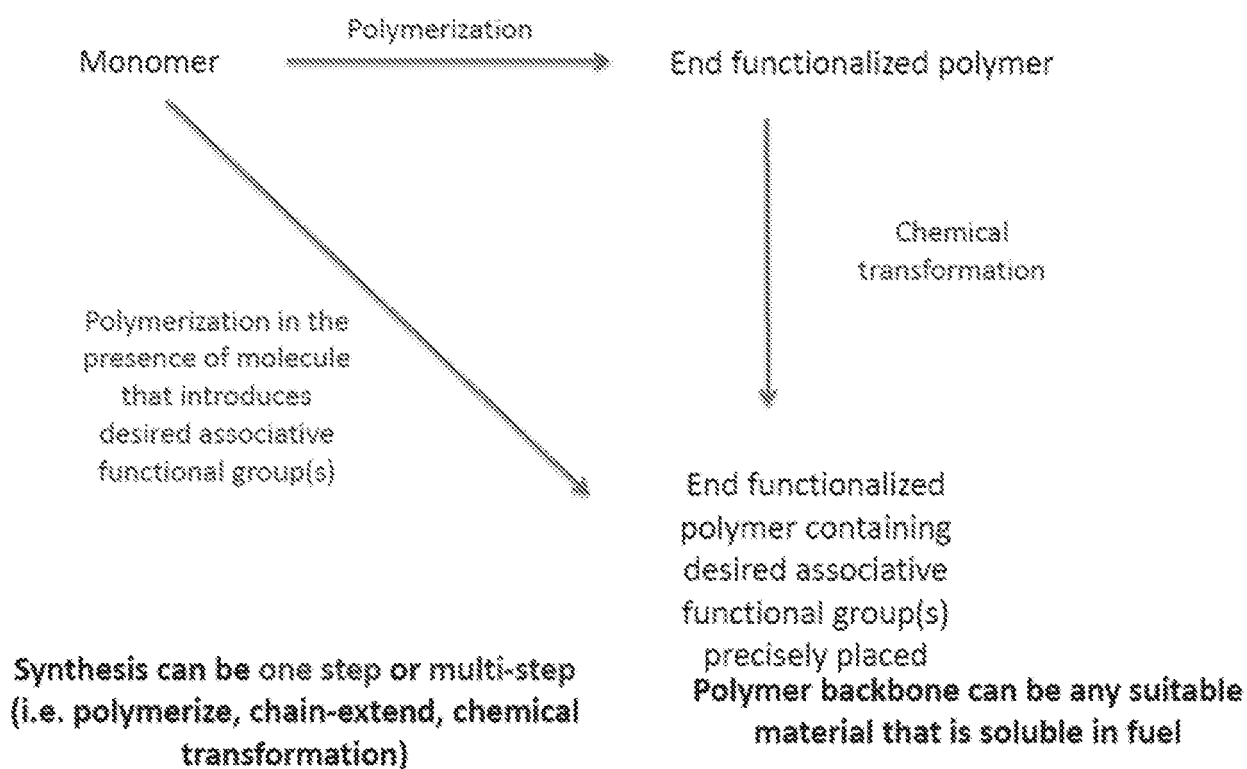
where



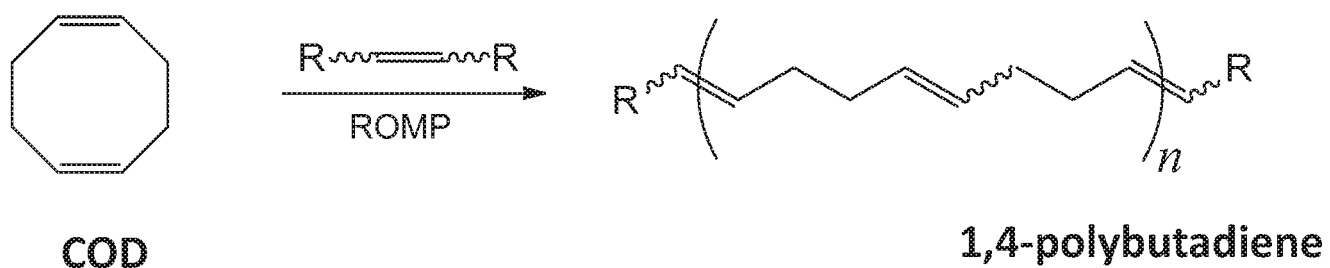
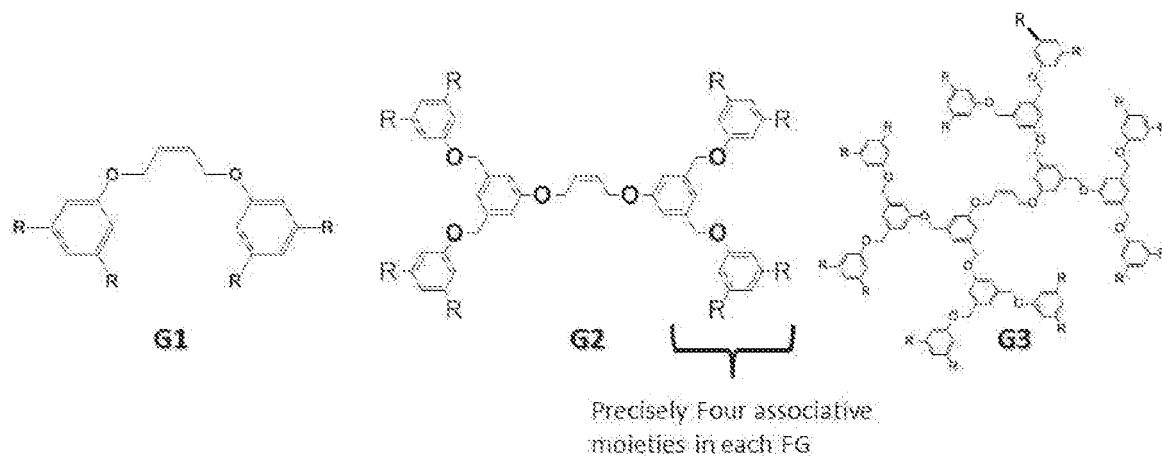
represents a generic
polymer backbone
soluble in fuel

FIG. 6

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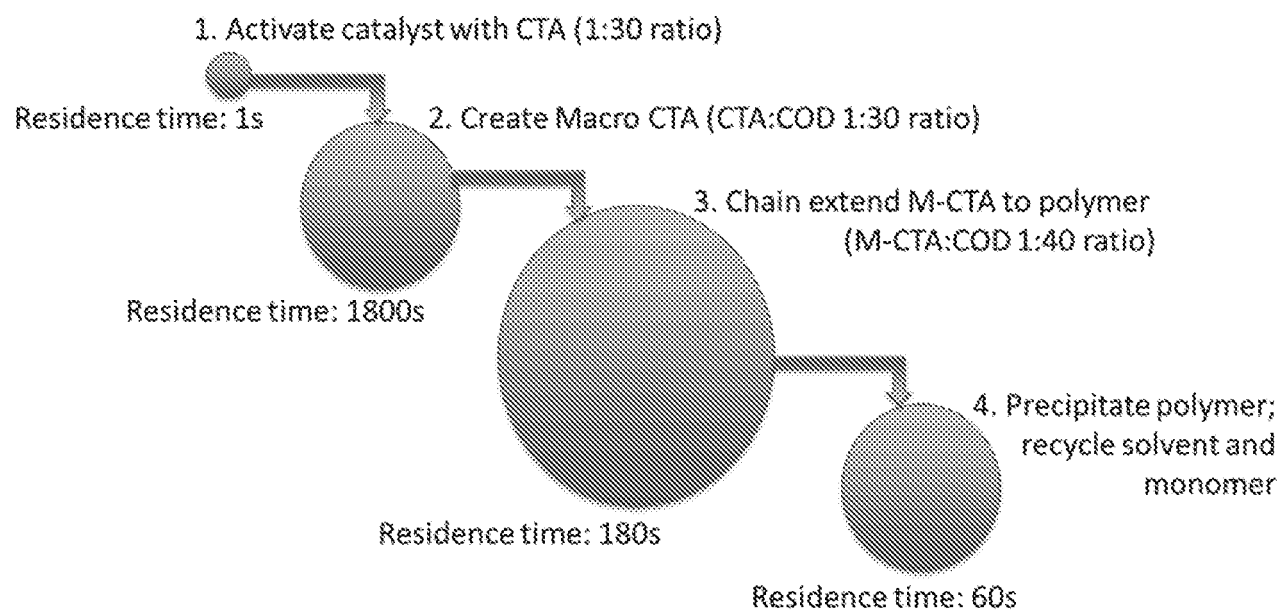
**FIG. 7**

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ROMP with Chain-transfer agent (CTA) $\rightarrow$ Telechelic**FIG. 8****FIG. 9**

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Cascade of CSTRs:

**FIG. 10**

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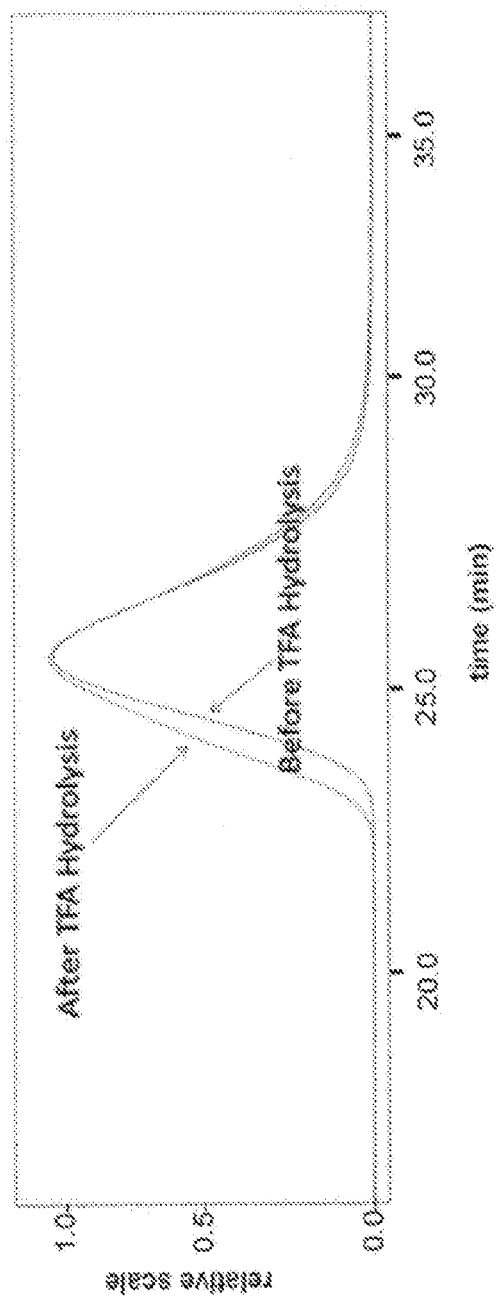


FIG. 11

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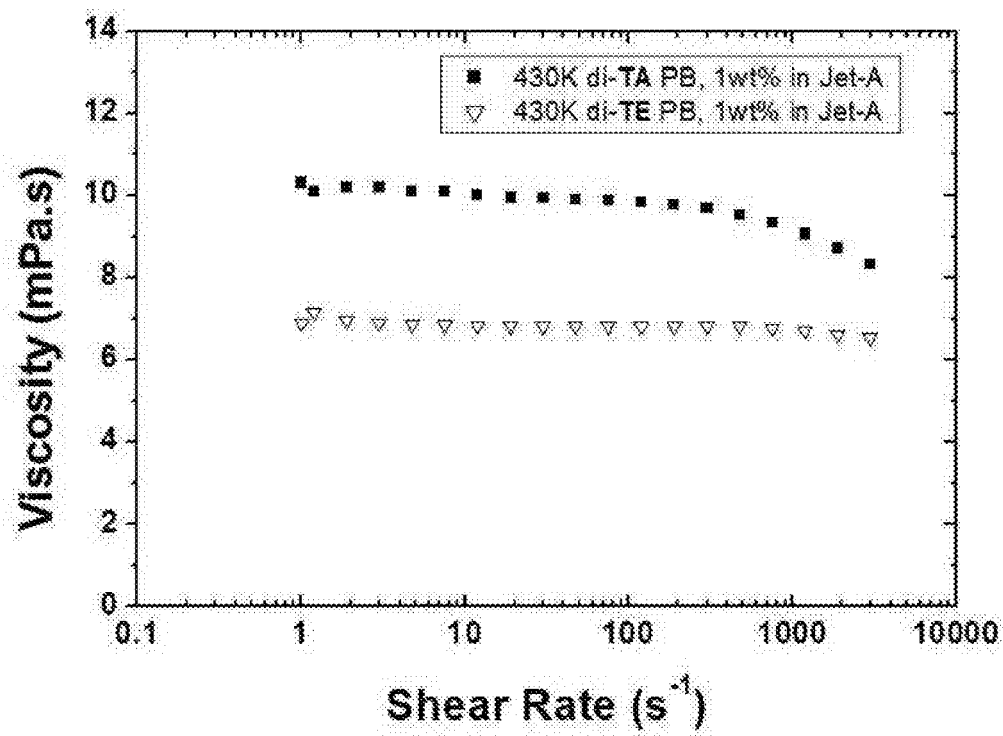


FIG. 12

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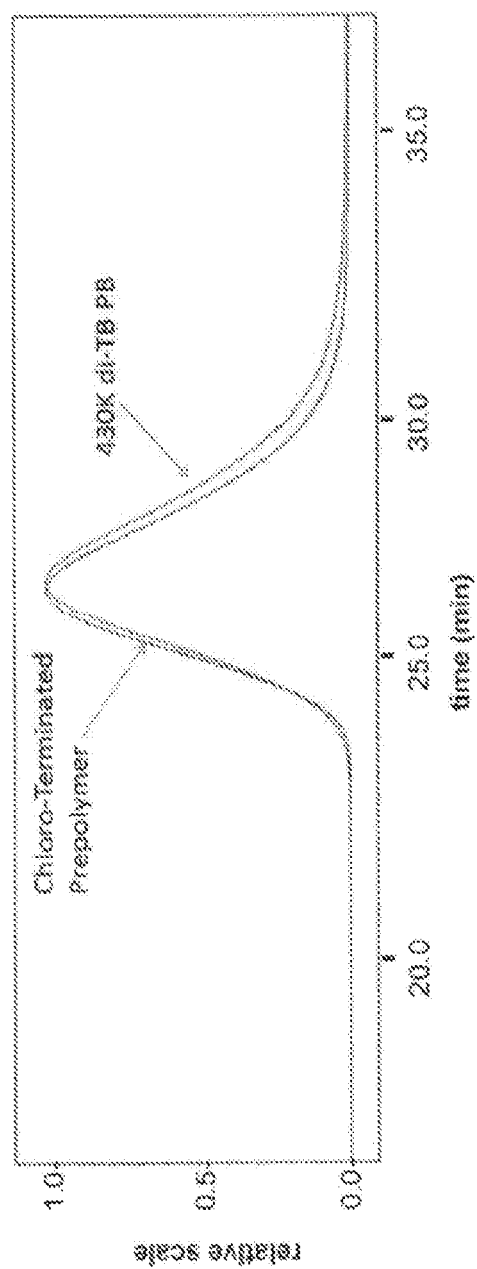


FIG. 13

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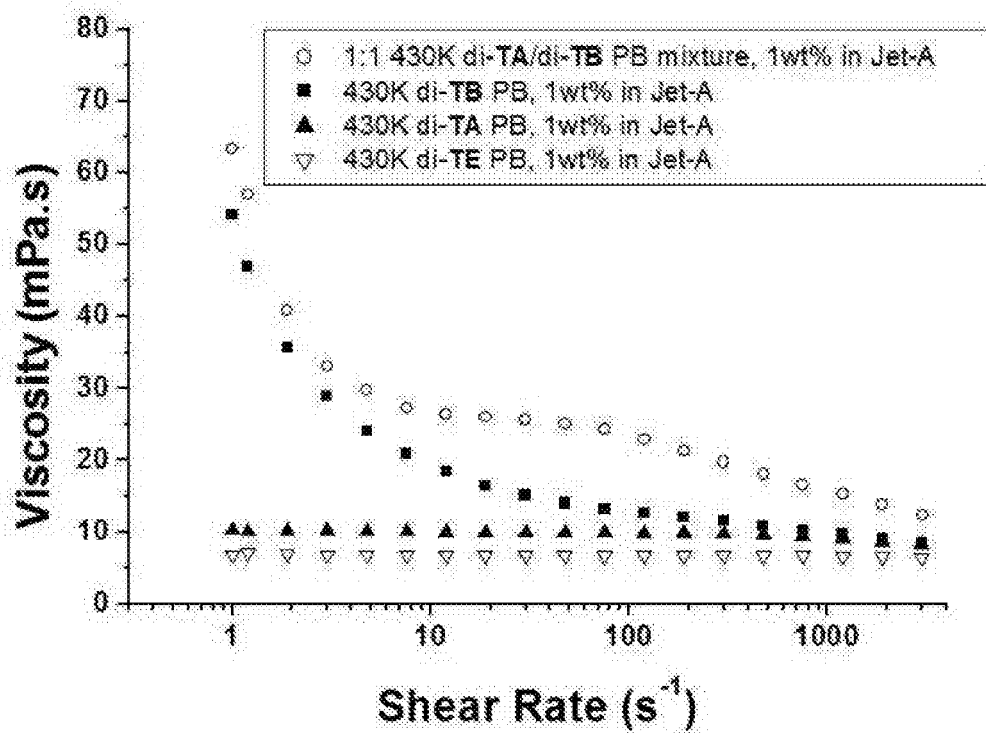
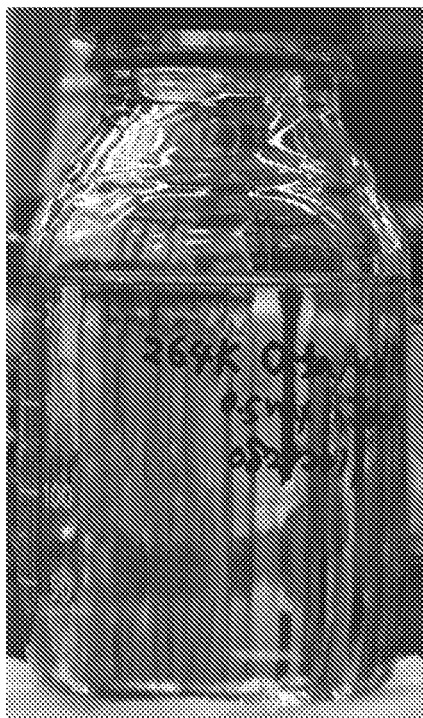
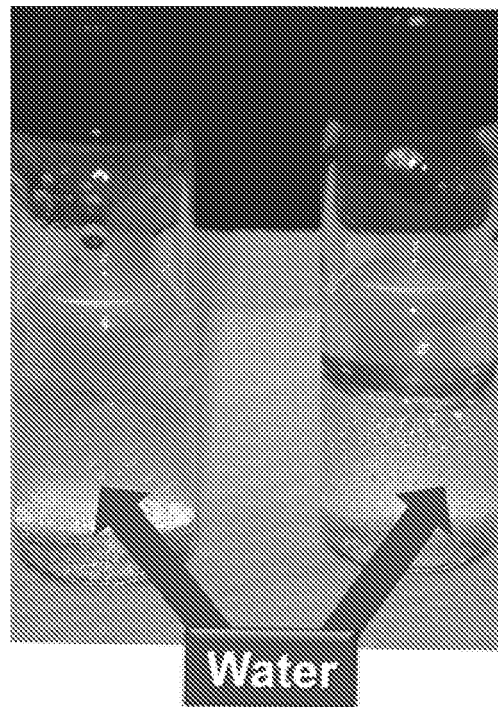
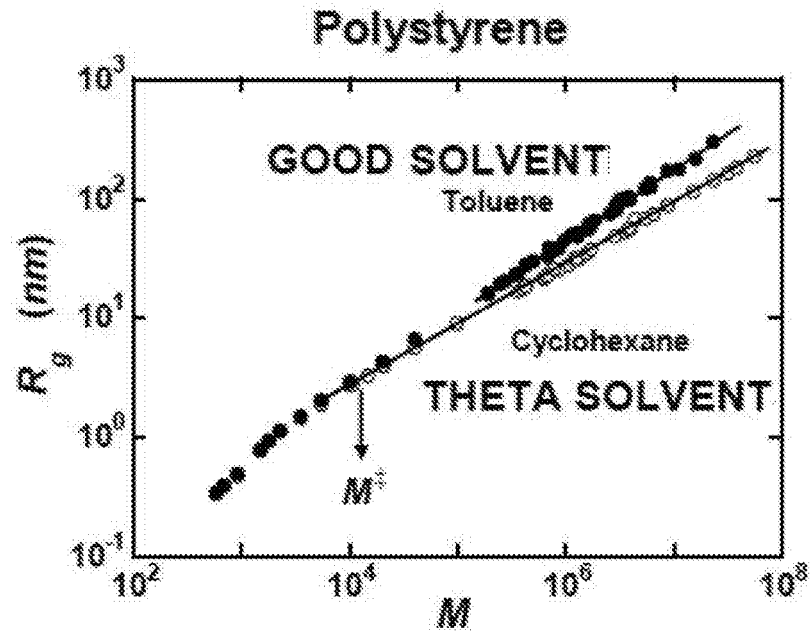


FIG. 14

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**A****B****FIG. 15**

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$$R_g = M^\nu \quad M \gg M^z$$

$\nu = 0.5$ theta ; $\nu = 0.59$ good

FIG. 16

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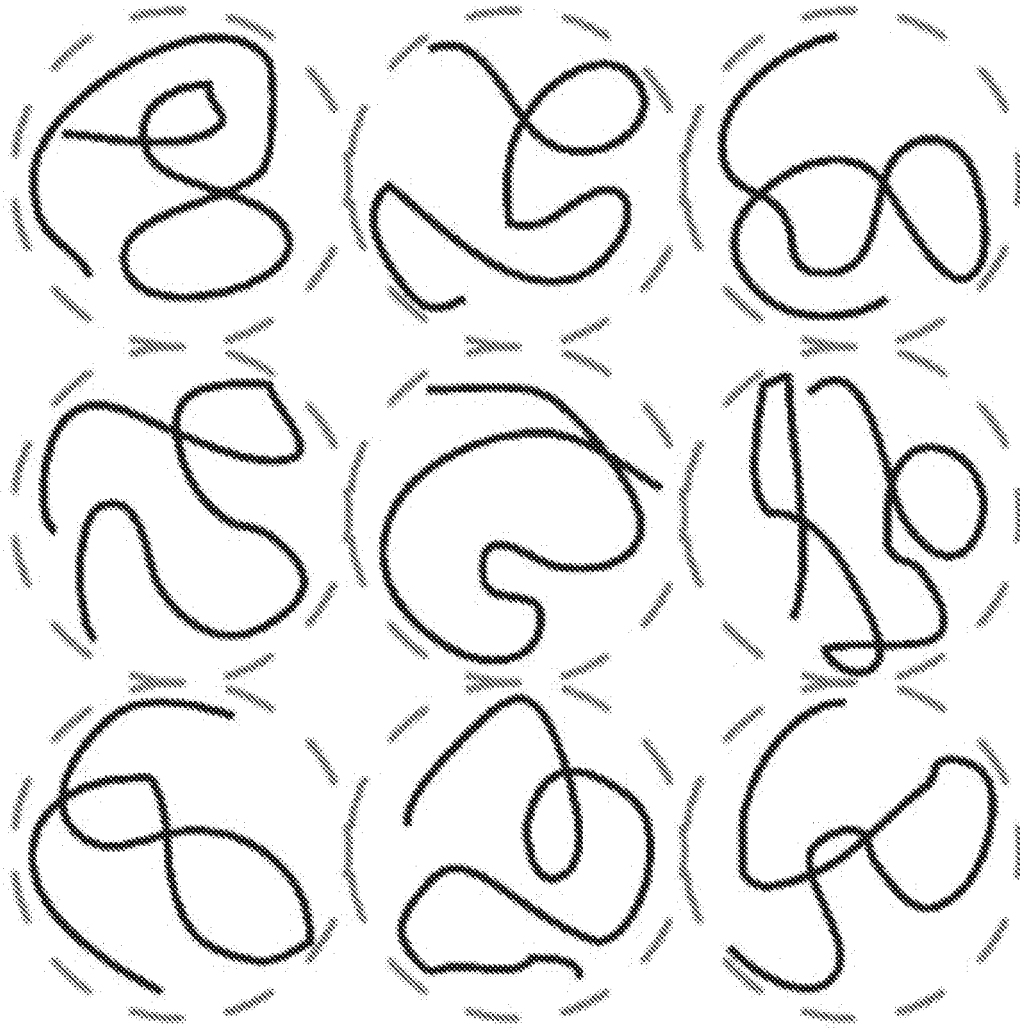


FIG. 17

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Synthesis of Octa-Functional *tert*-Butyl Ester CTA

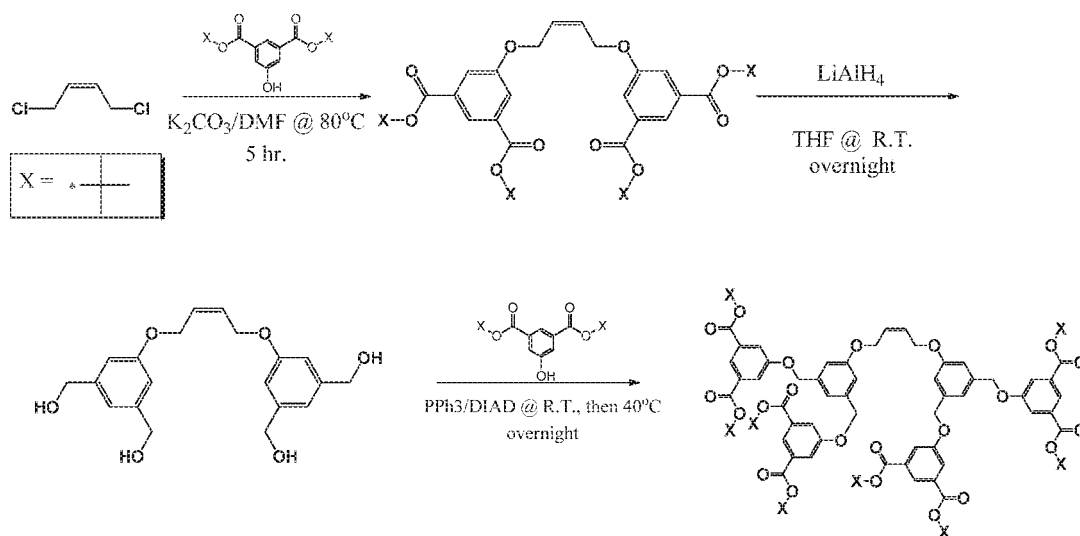


FIG. 18

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Synthesis of Octa-Functional Chloro CTA

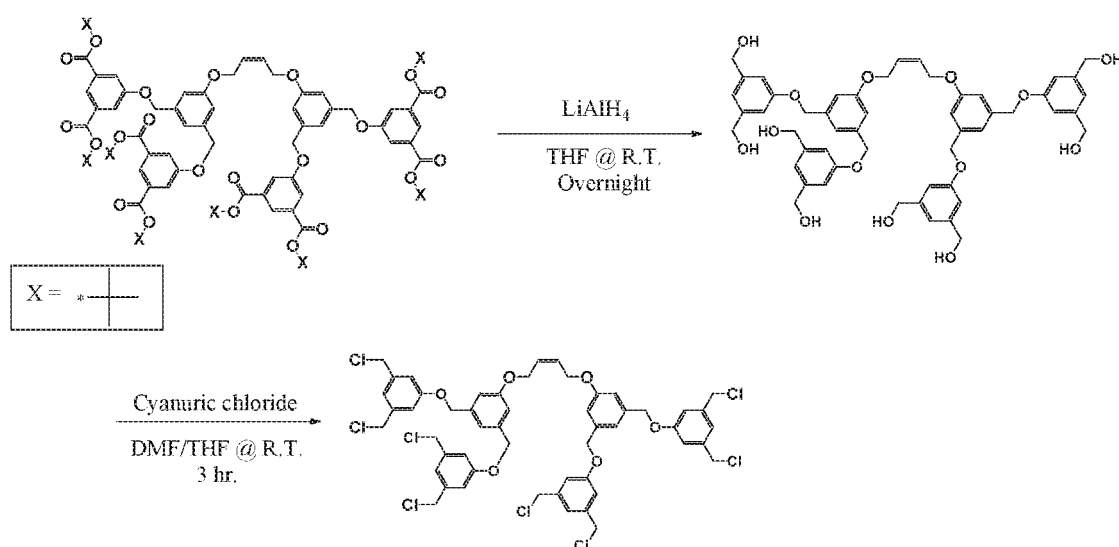


FIG. 19

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Copper-catalyzed azide-alkyne cycloaddition (CuAAC)

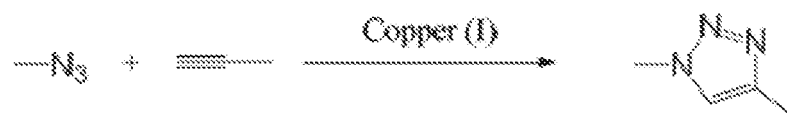
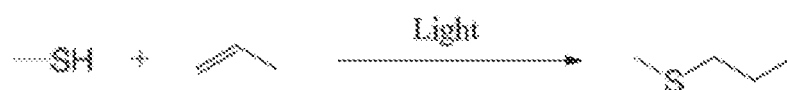
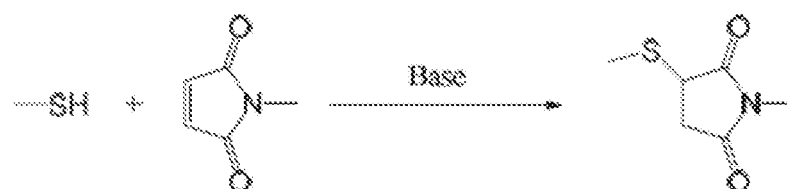


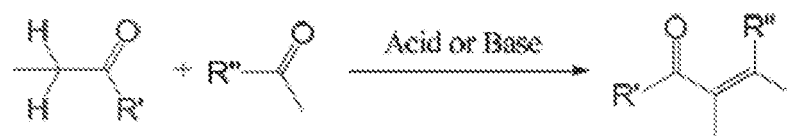
Photo thiol-ene



Michael-type thiol-maleimide



Aldol condensation



NHS

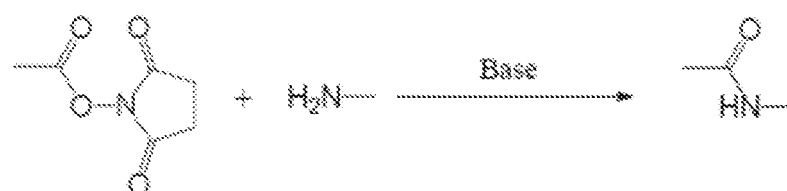
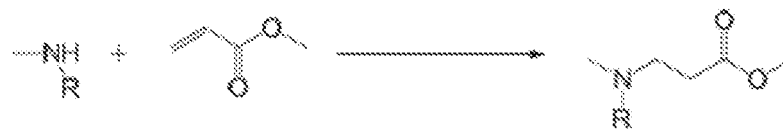


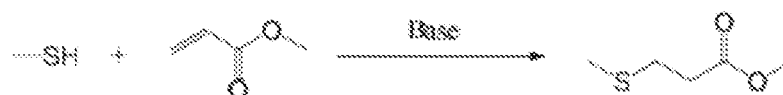
FIG. 20

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Michael addition with amine



Michael addition with thiol



Maleimide [Diels-Alder]

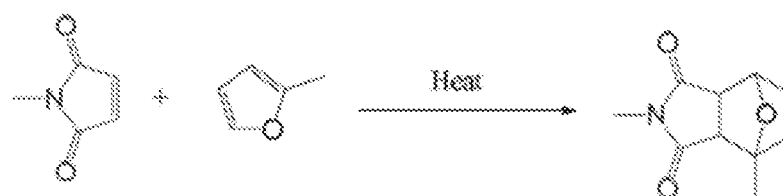


FIG. 21

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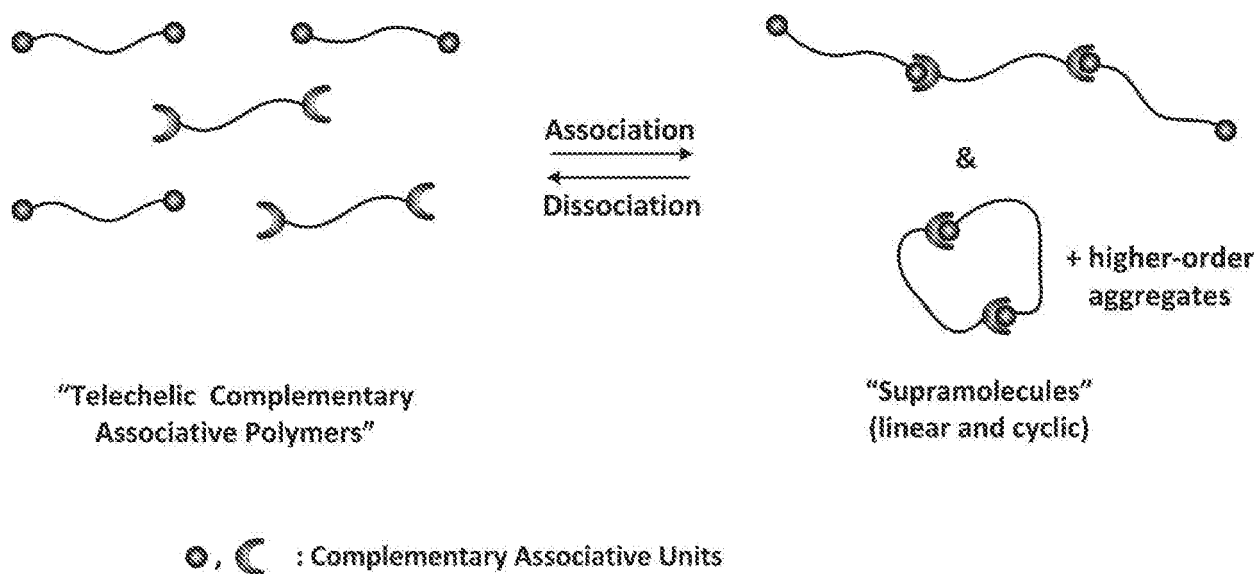


Fig. 22

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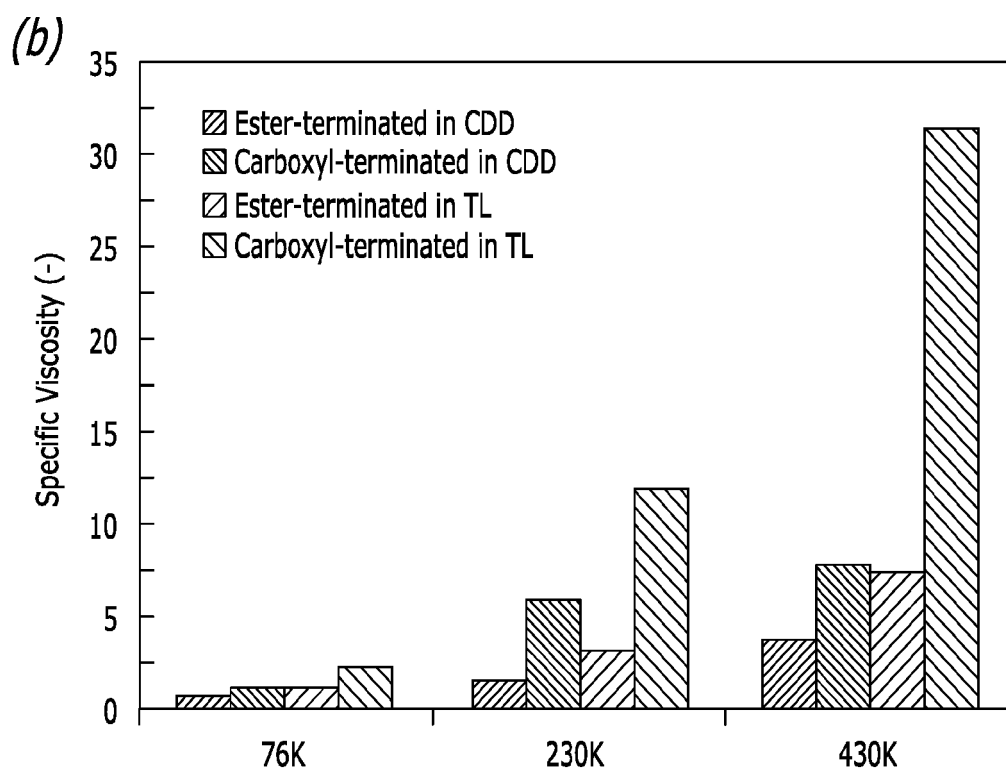
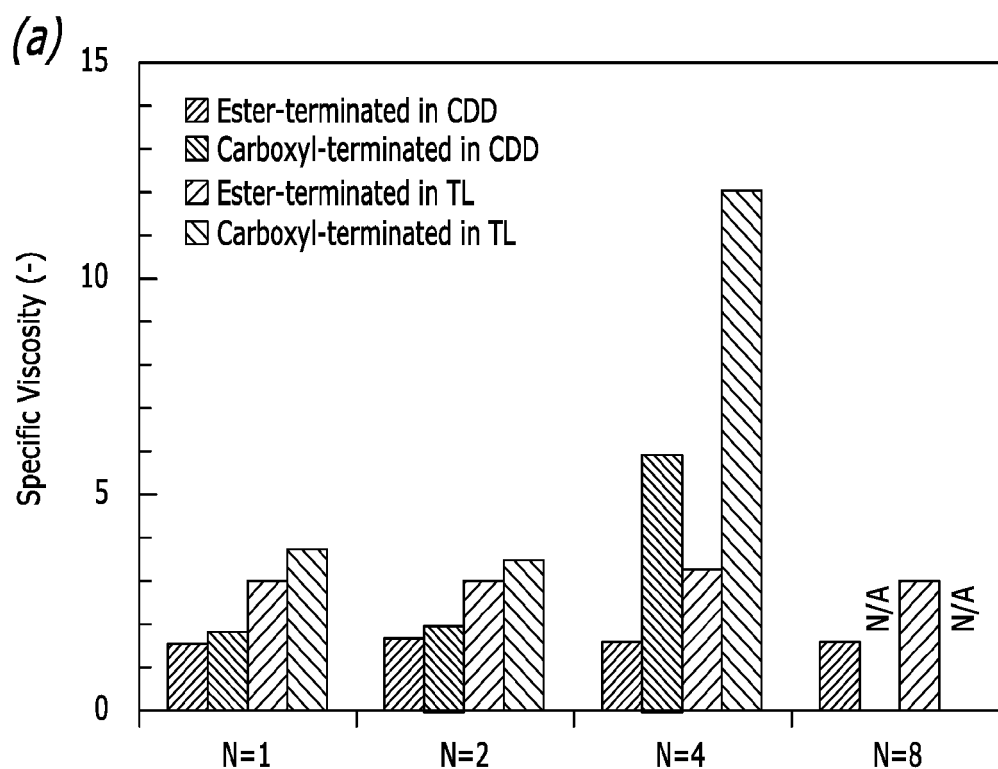


FIG. 23

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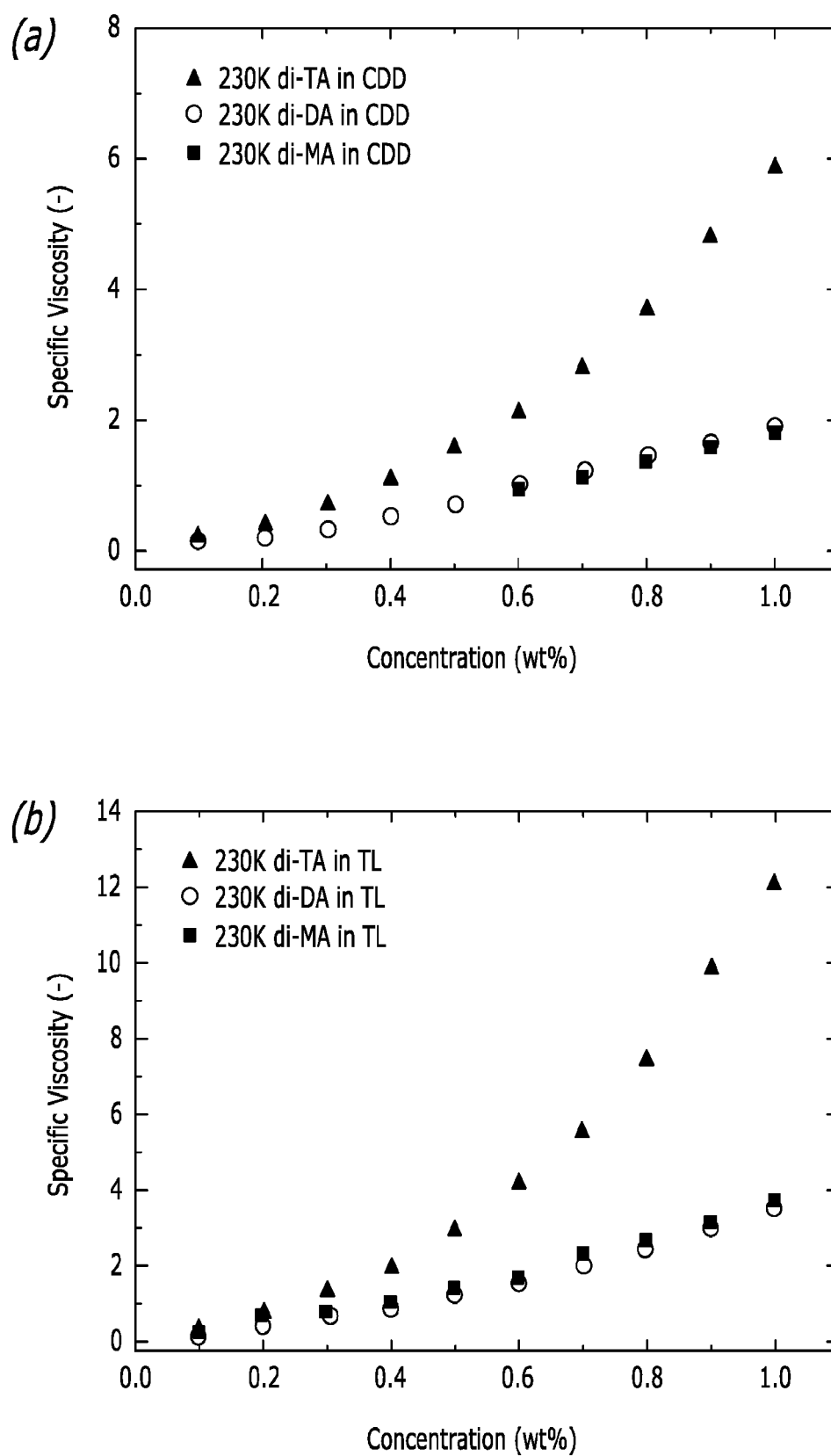


FIG. 24

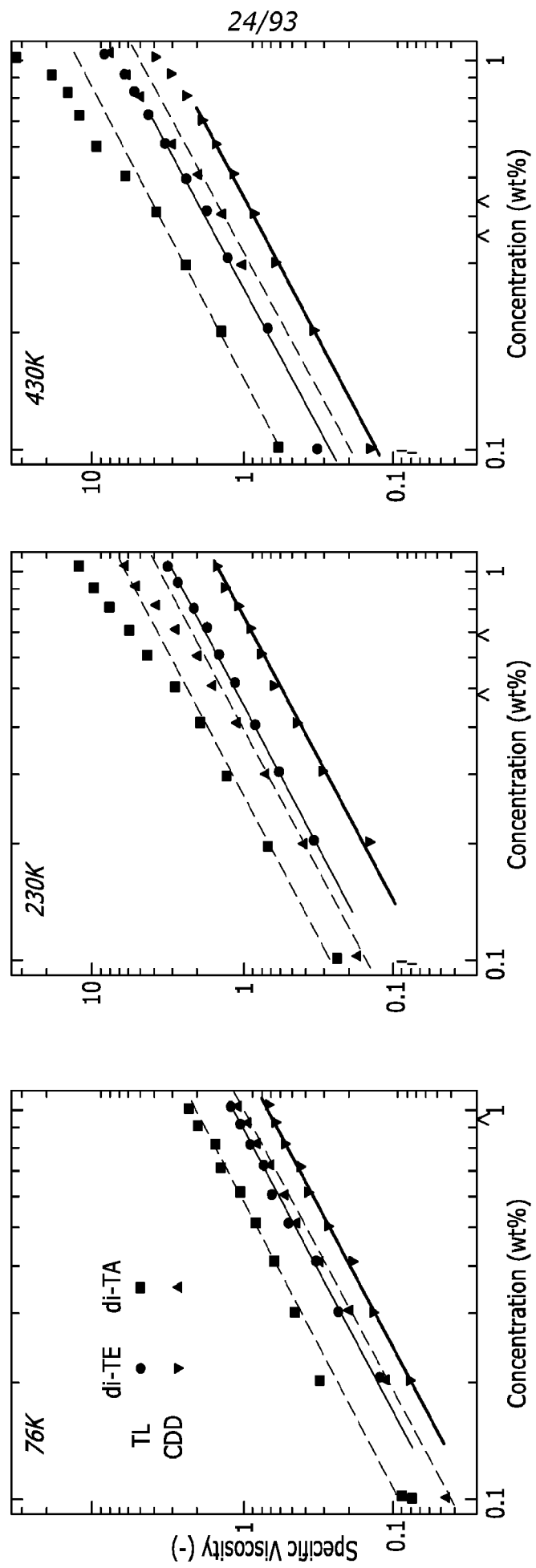


FIG. 25

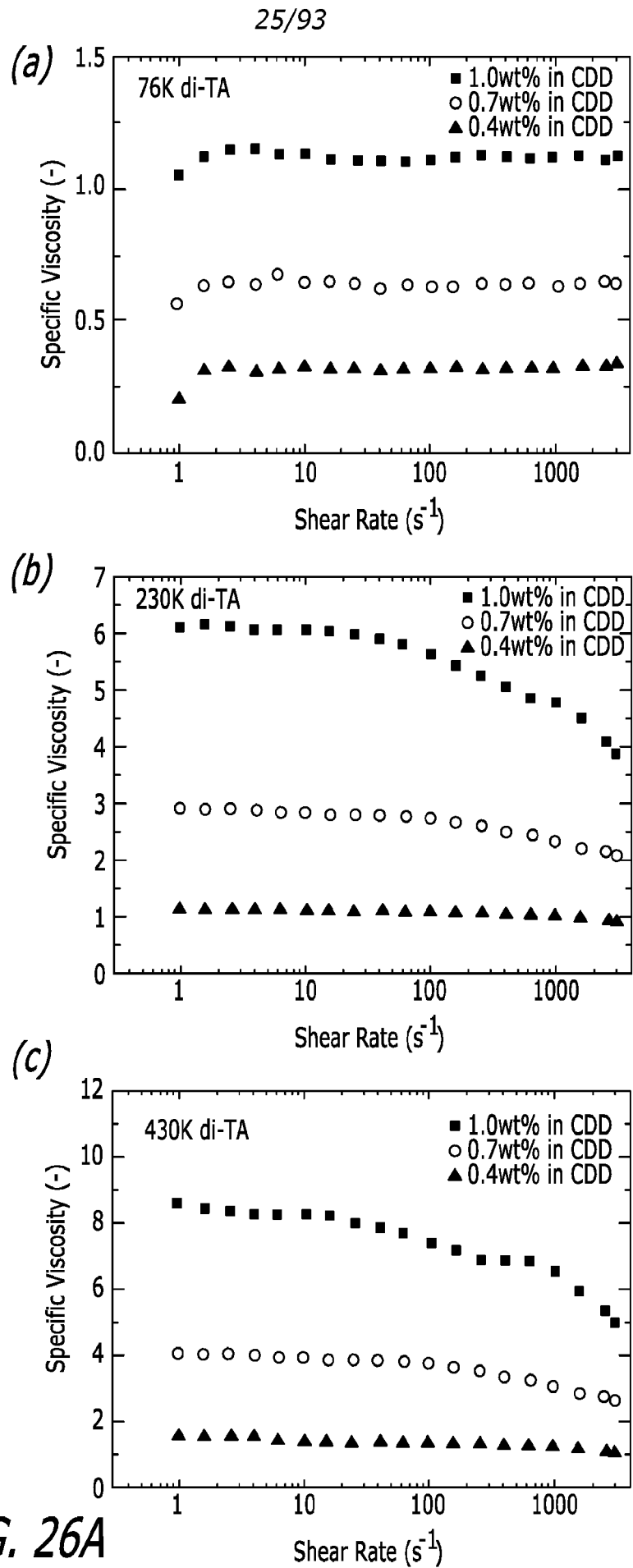


FIG. 26A

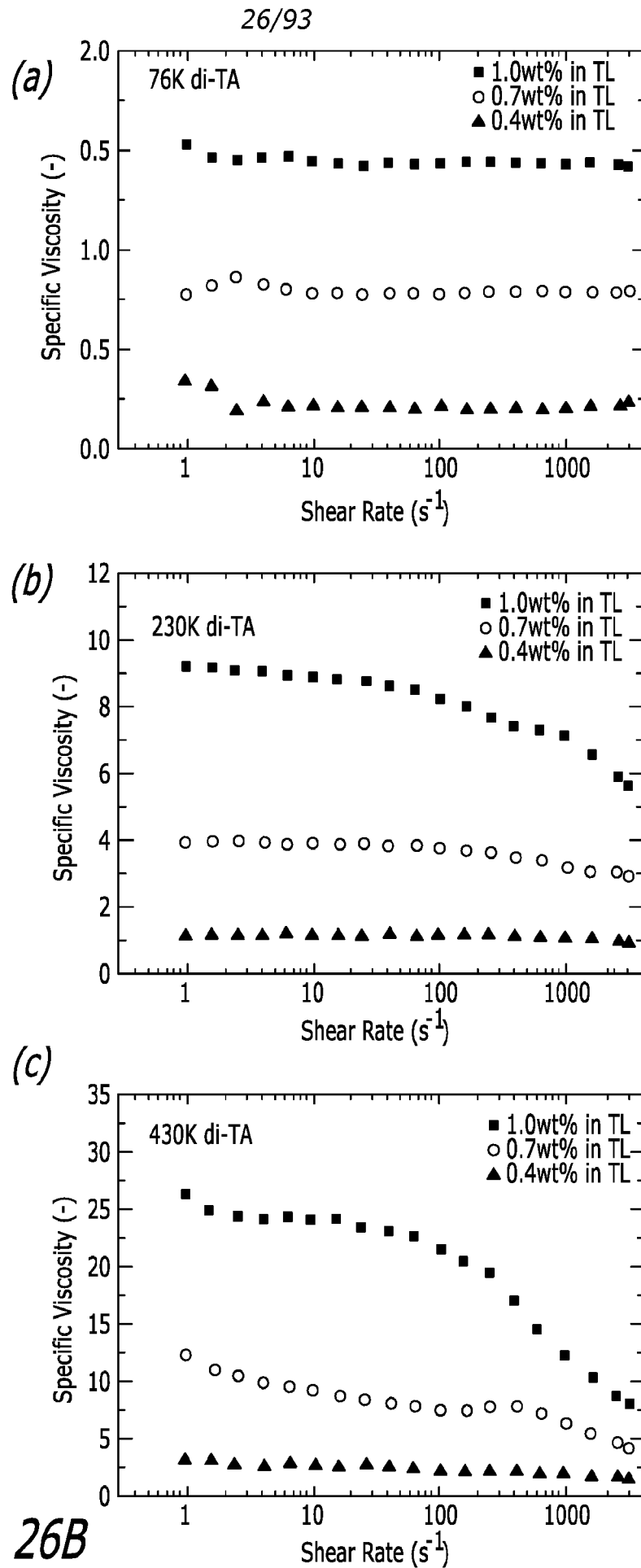


FIG. 26B

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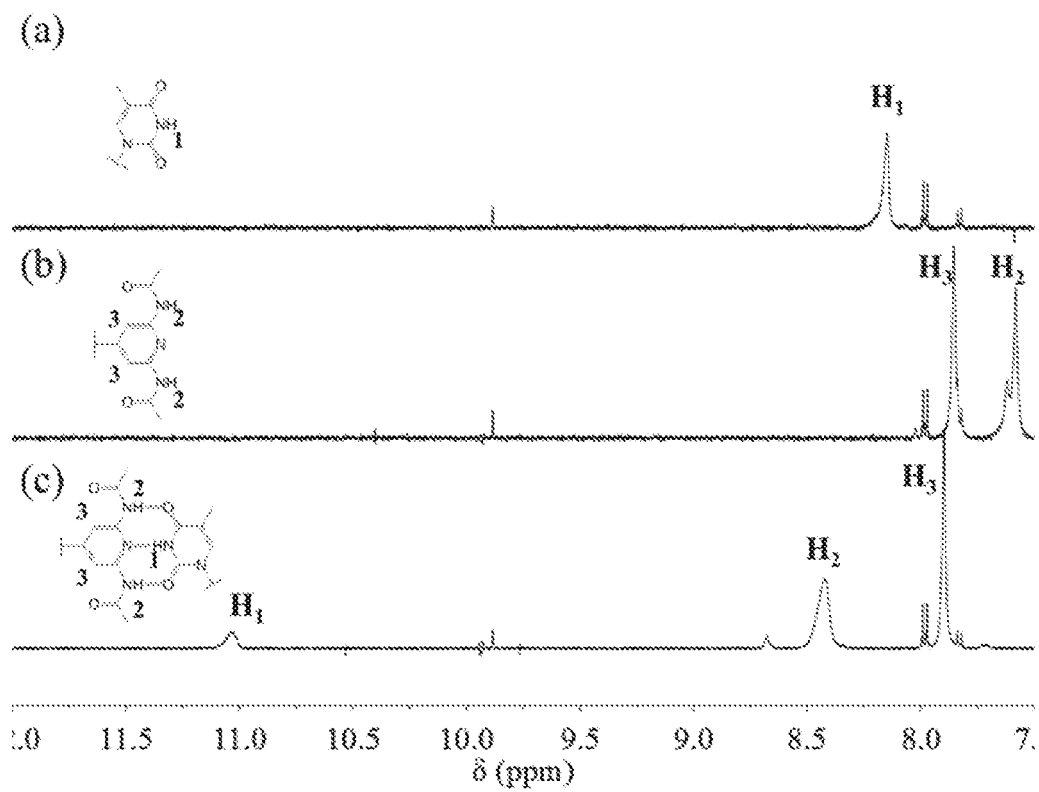


Fig. 27

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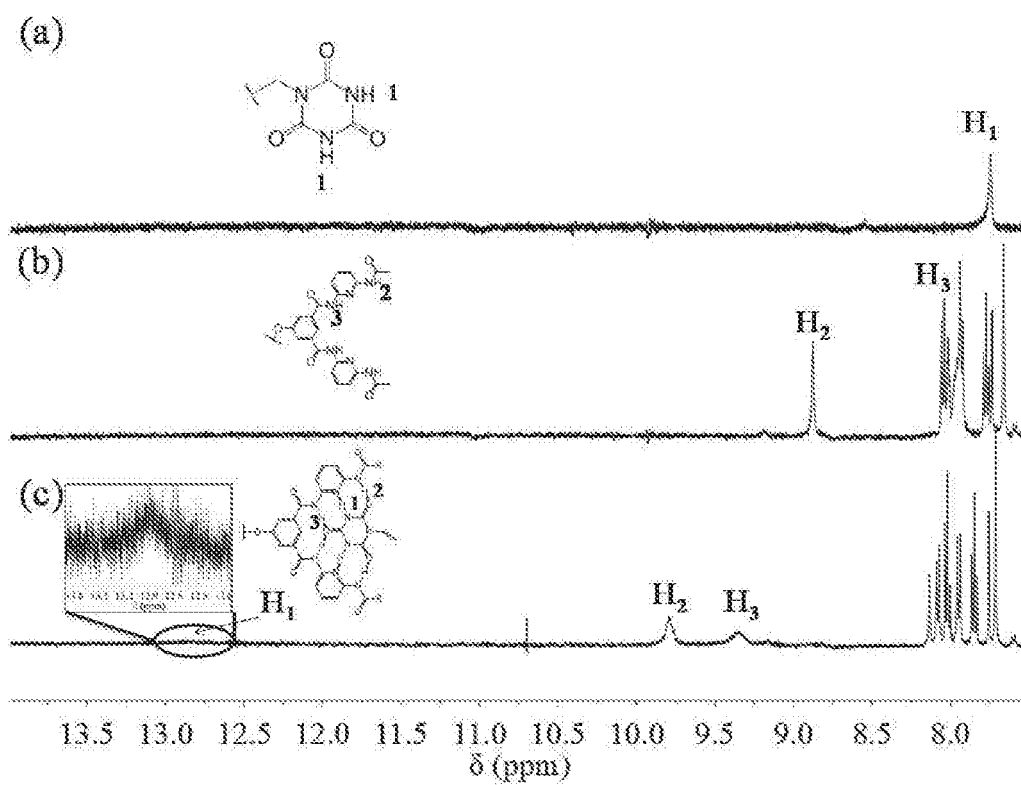


Fig. 28

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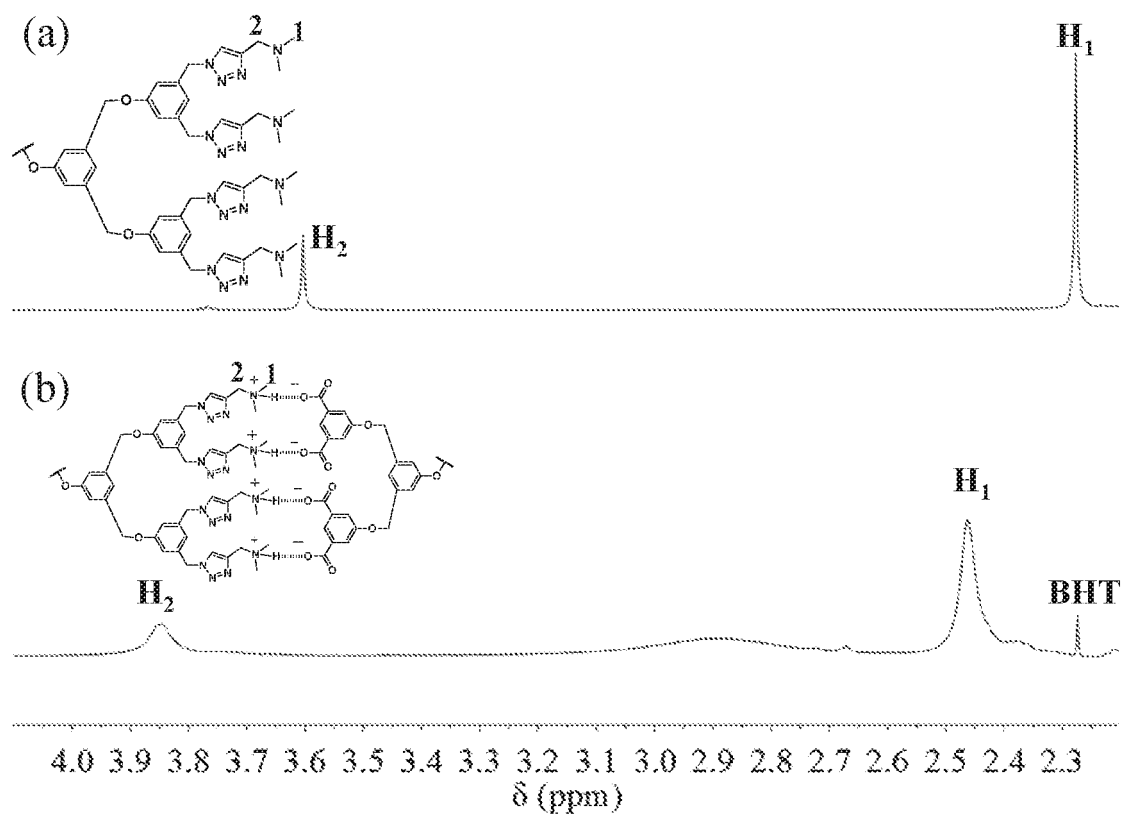


Fig. 29

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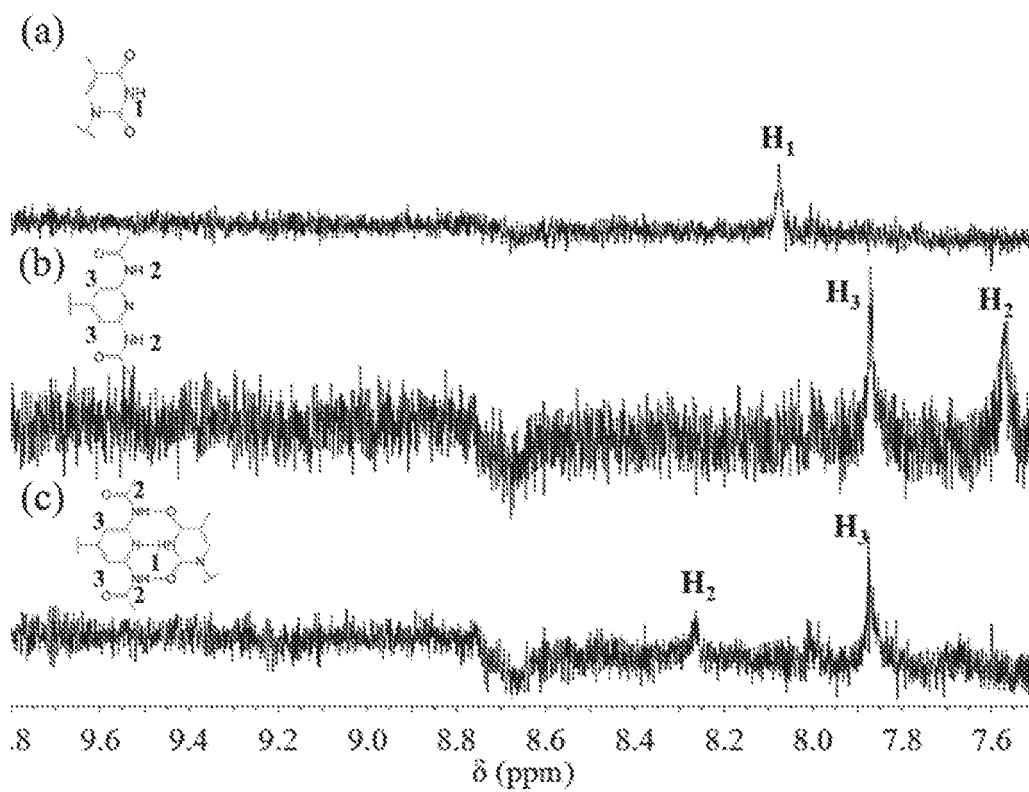


Fig. 30

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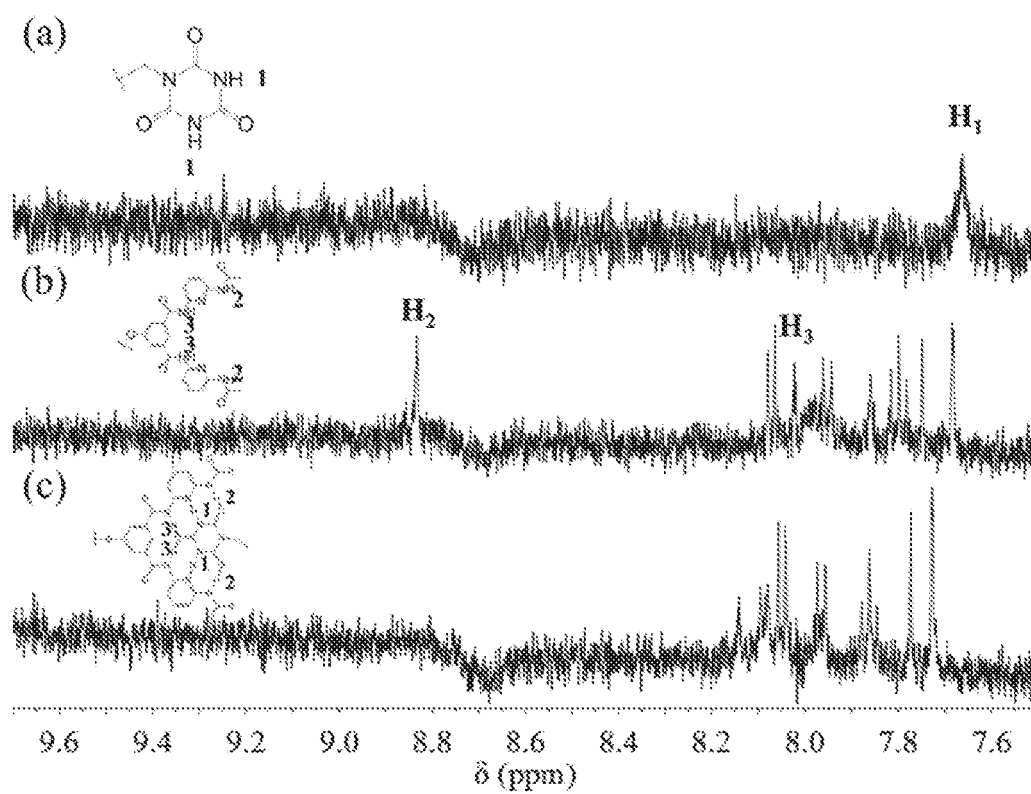


Fig. 31

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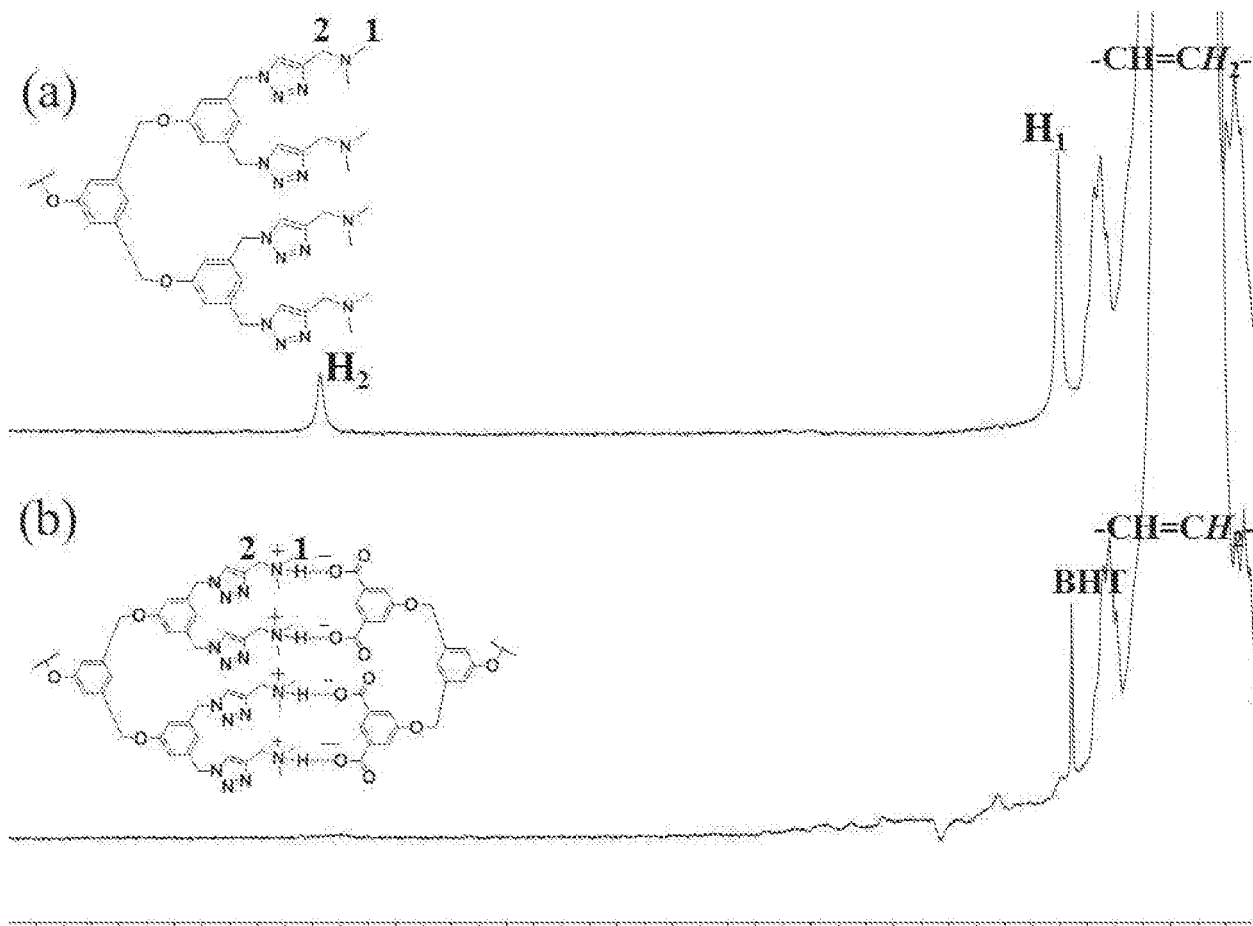


Fig. 32

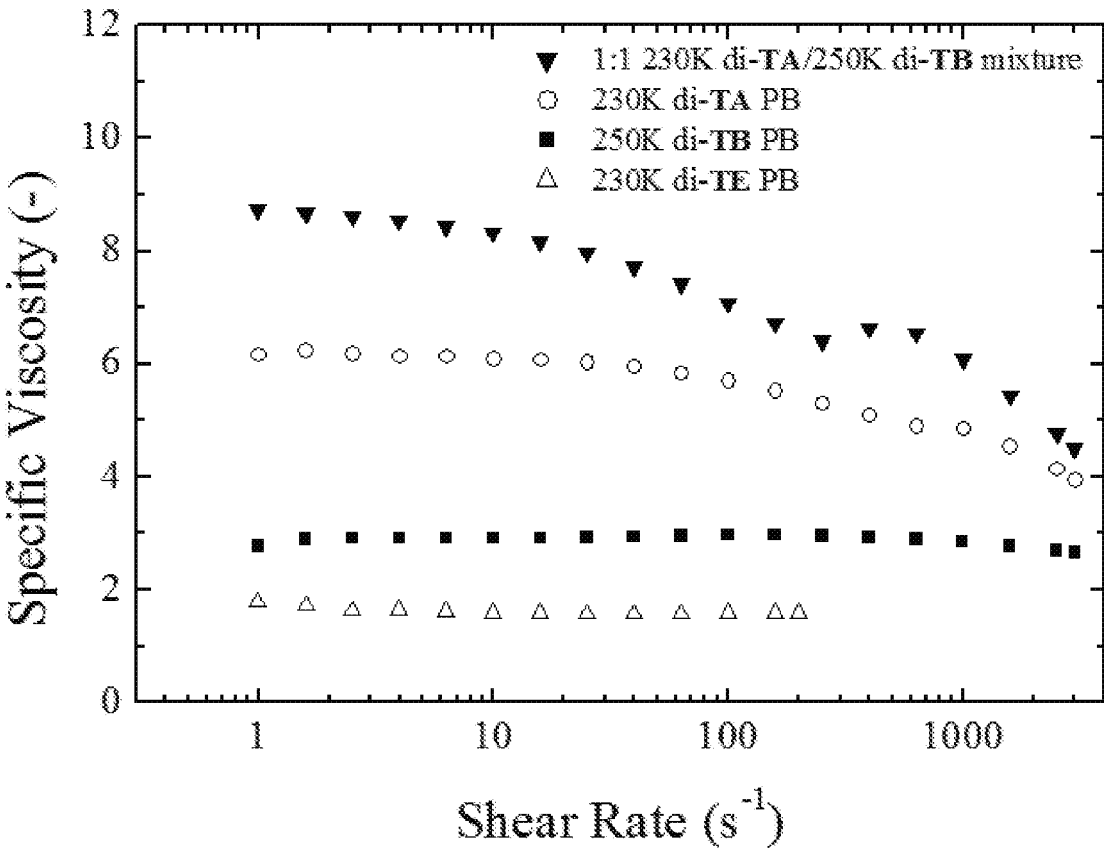


Fig. 33

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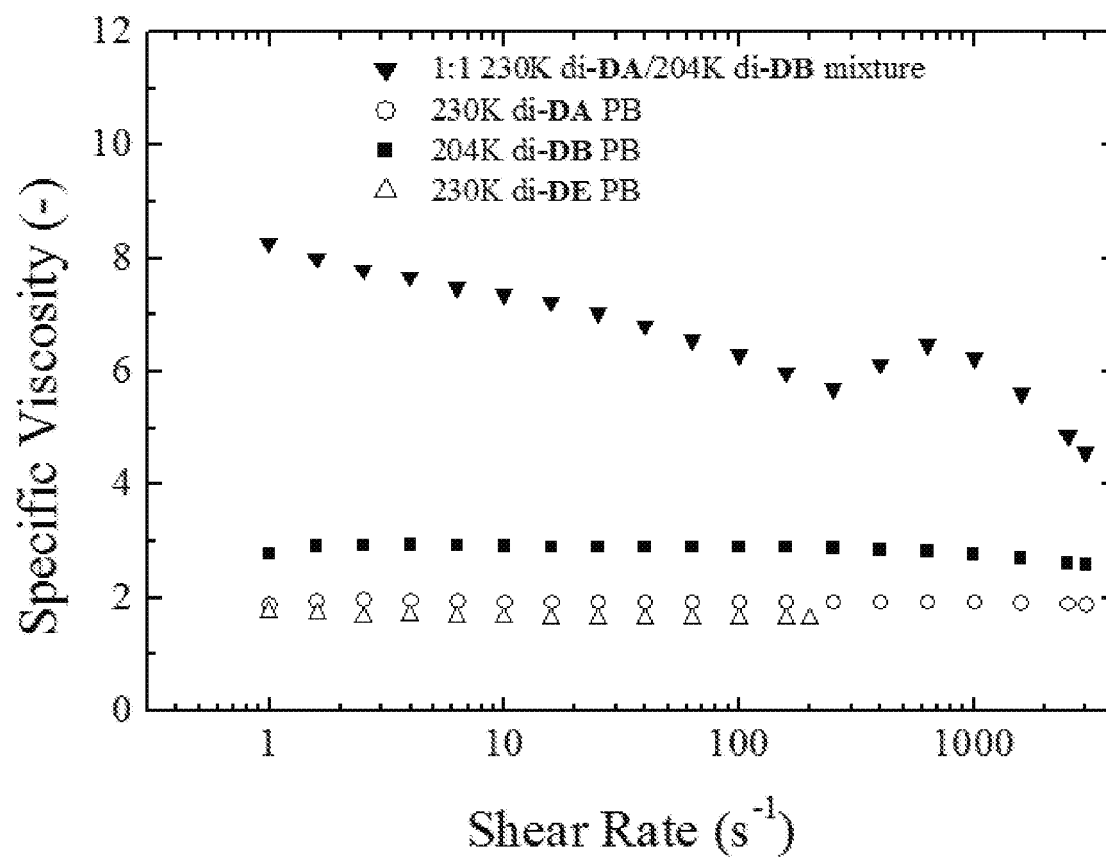


Fig. 34

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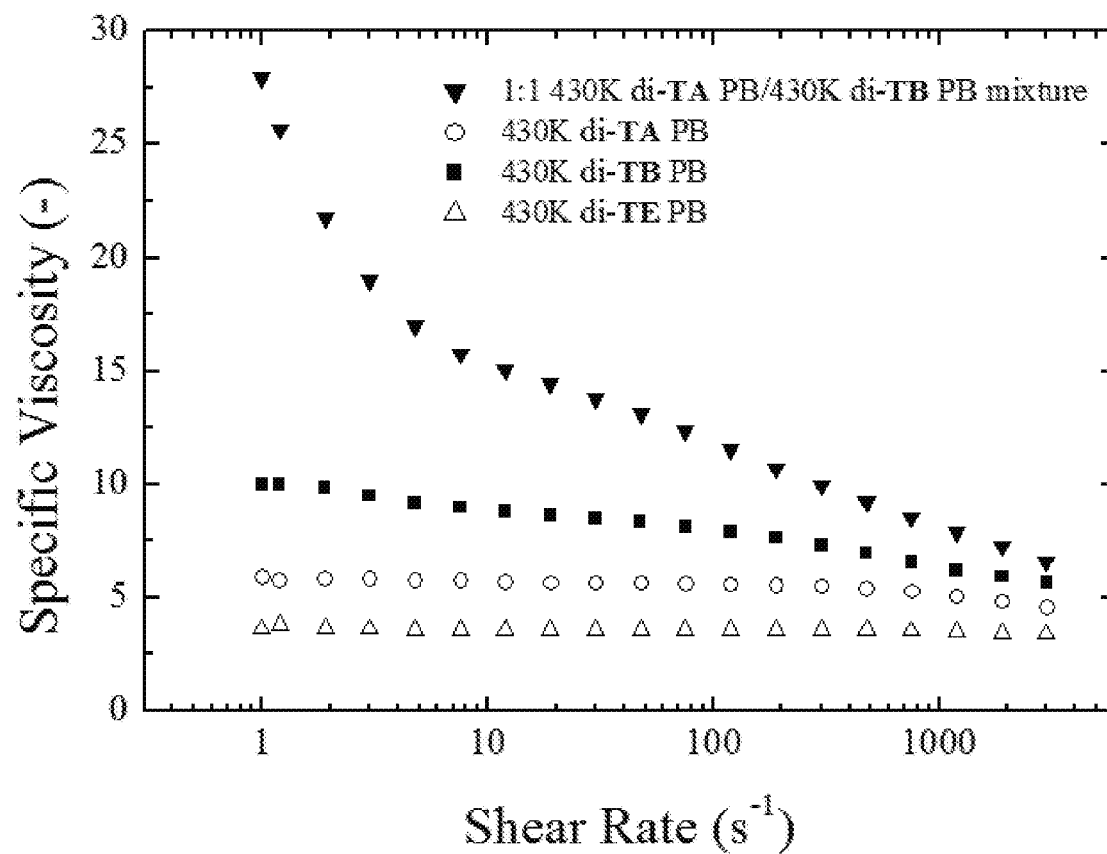
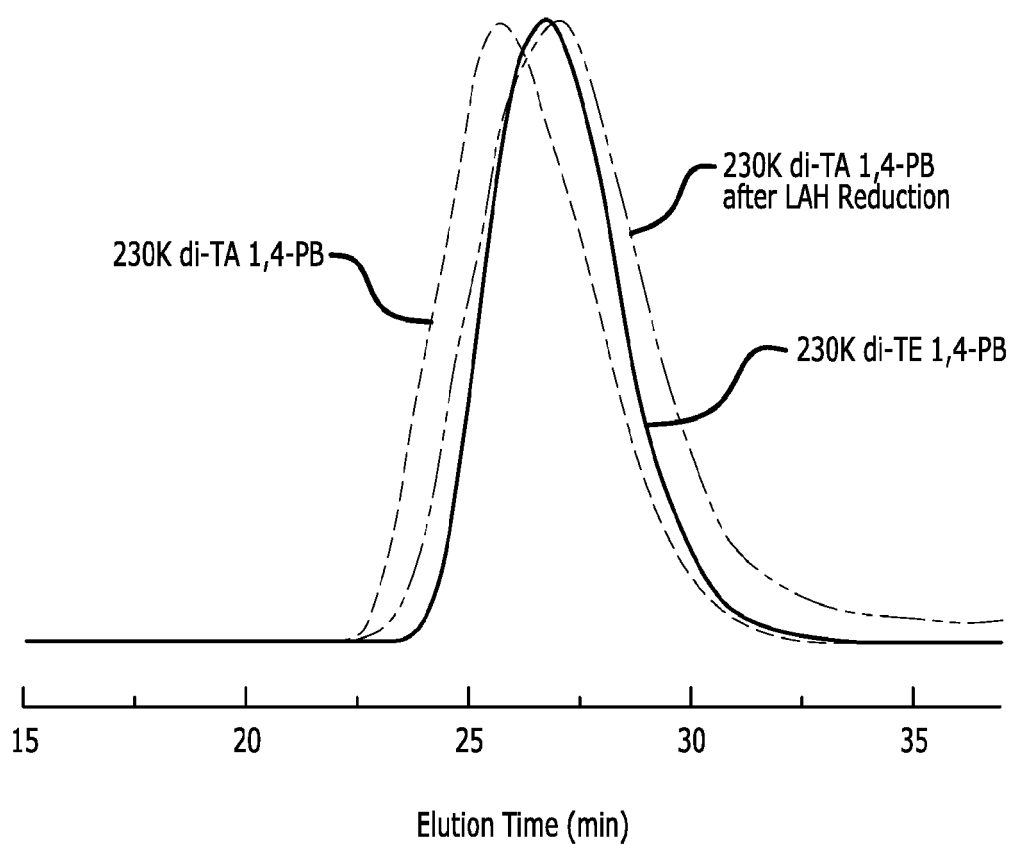


Fig. 35

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FIG. 36

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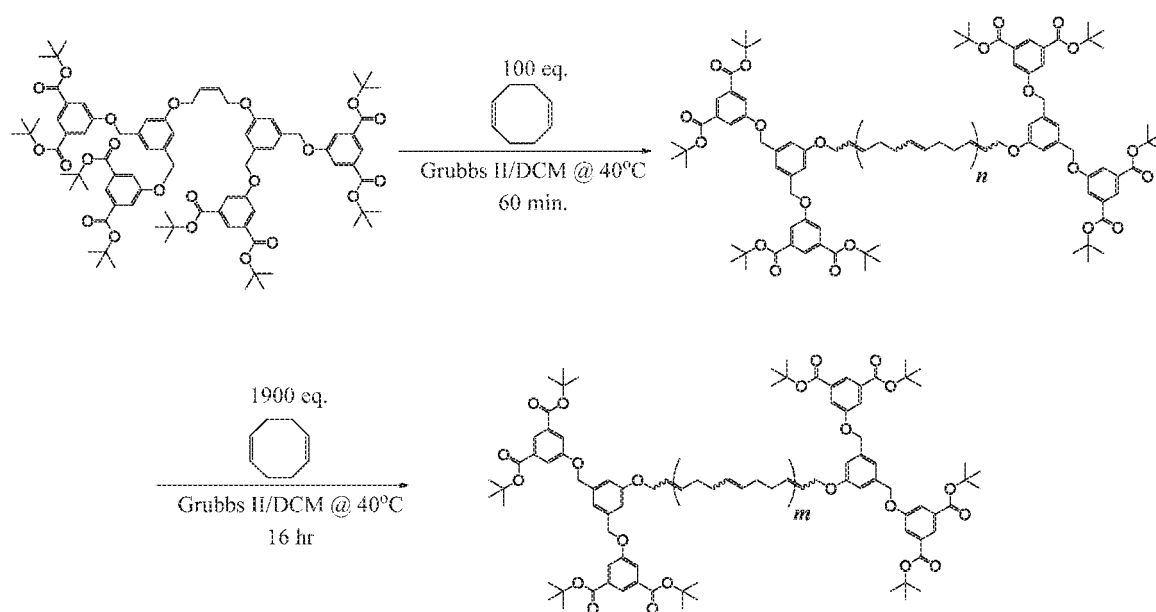


Fig. 37

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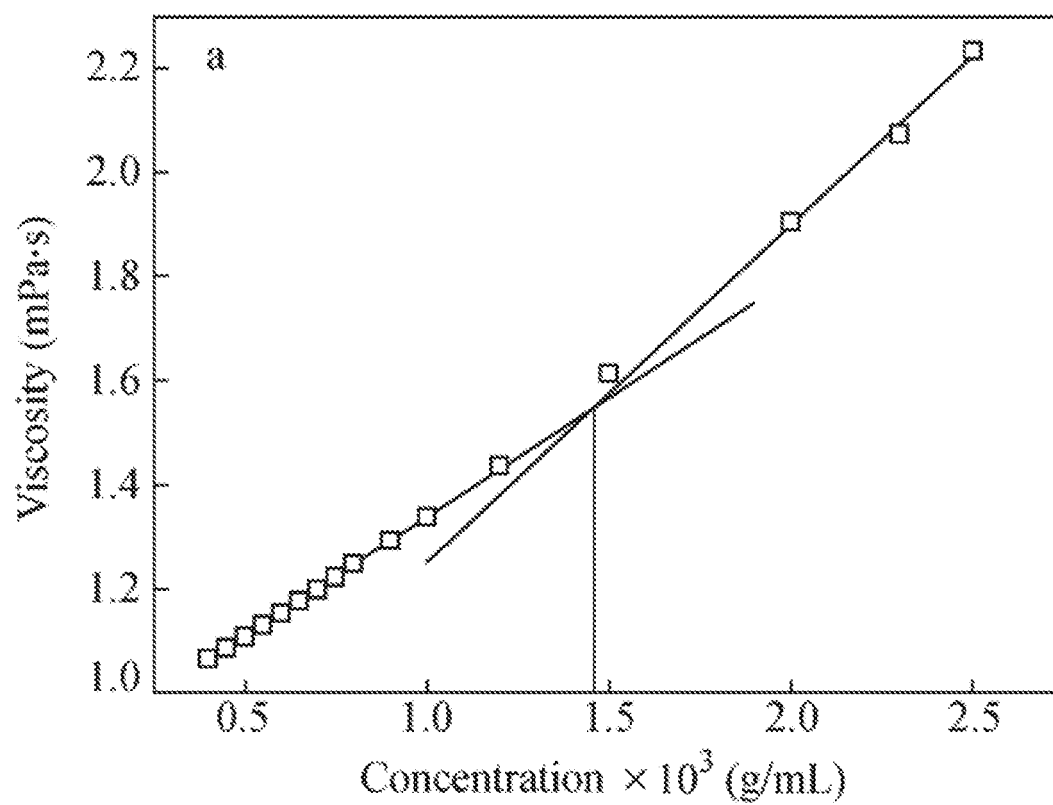
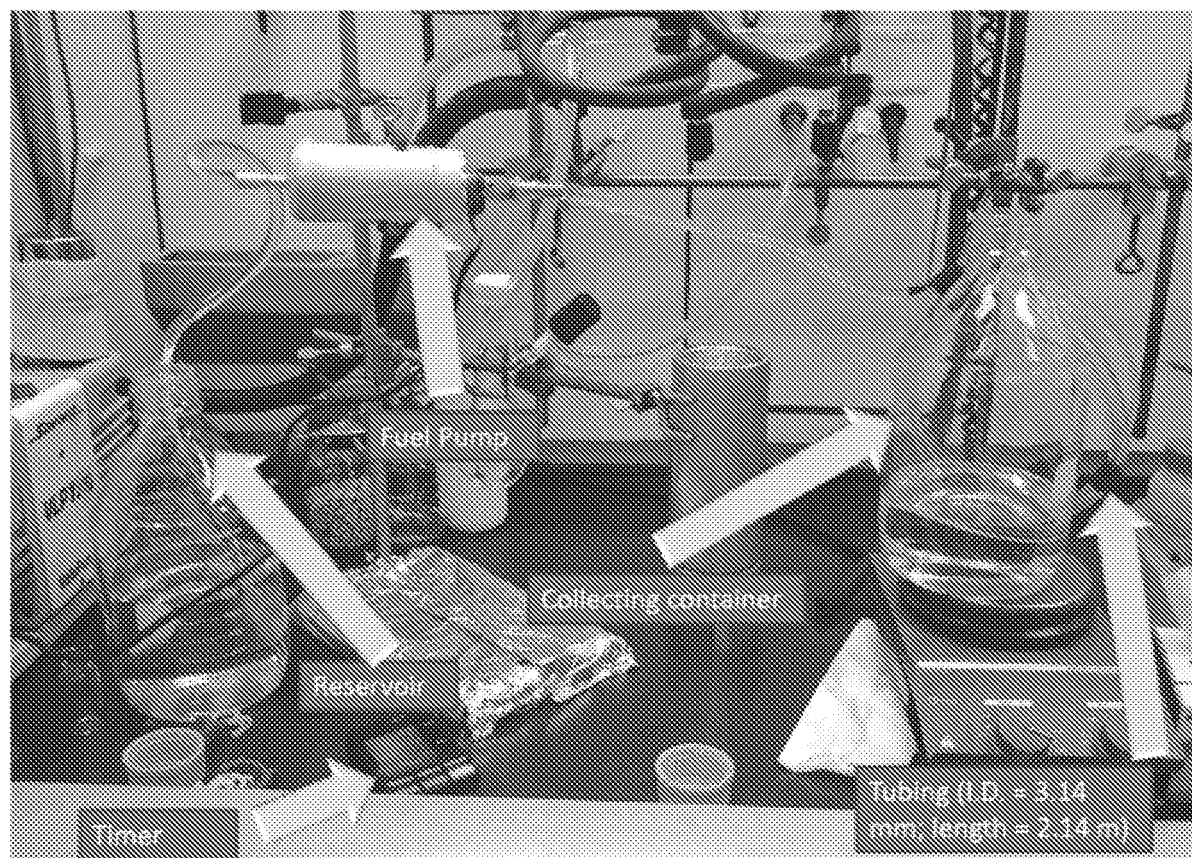


Fig. 38

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**FIG. 39A**

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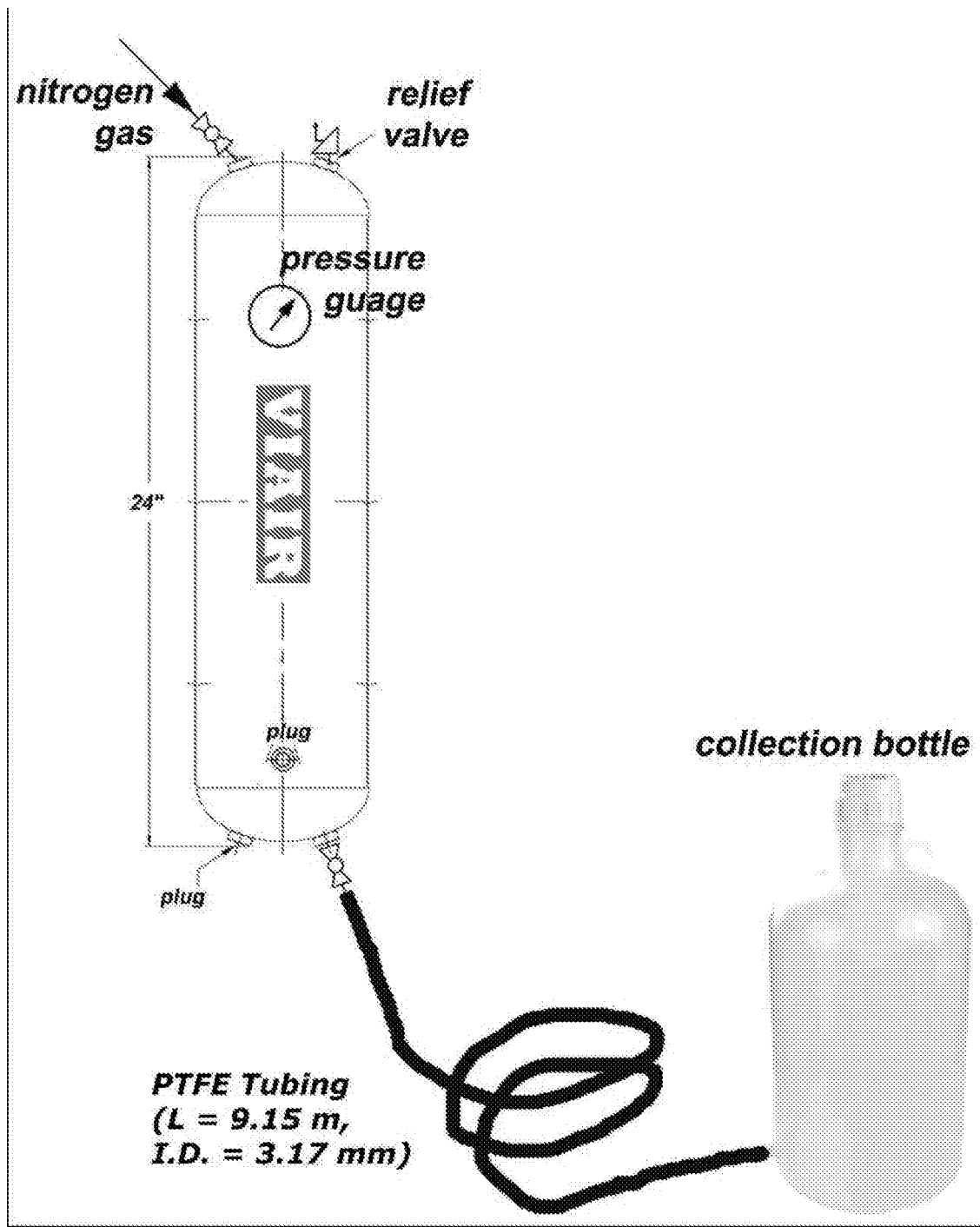
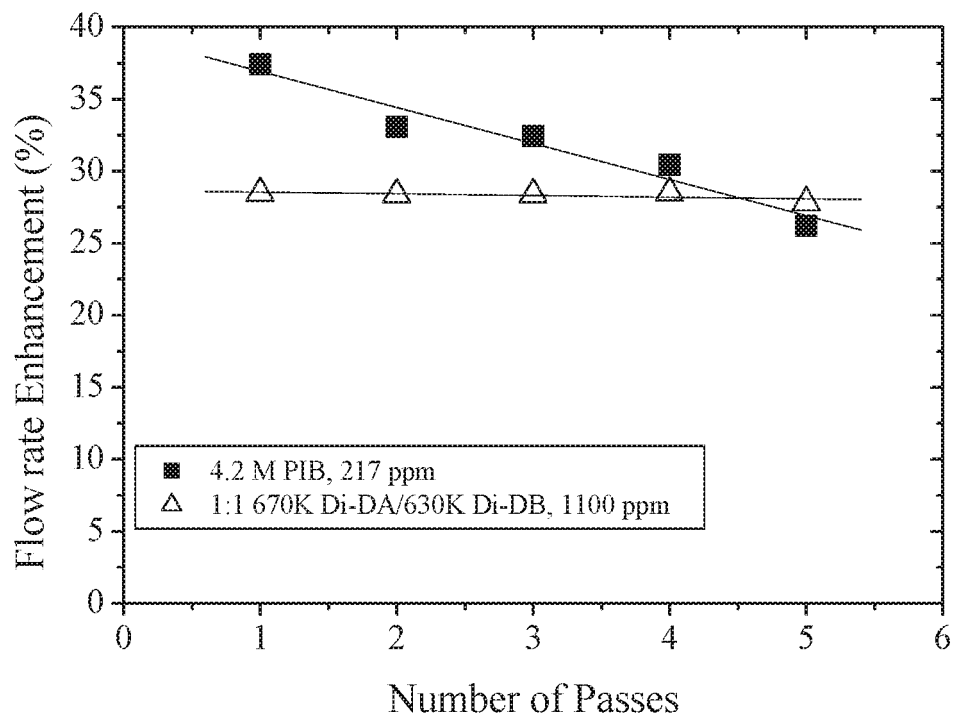


FIG. 39B

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**FIG. 39C**

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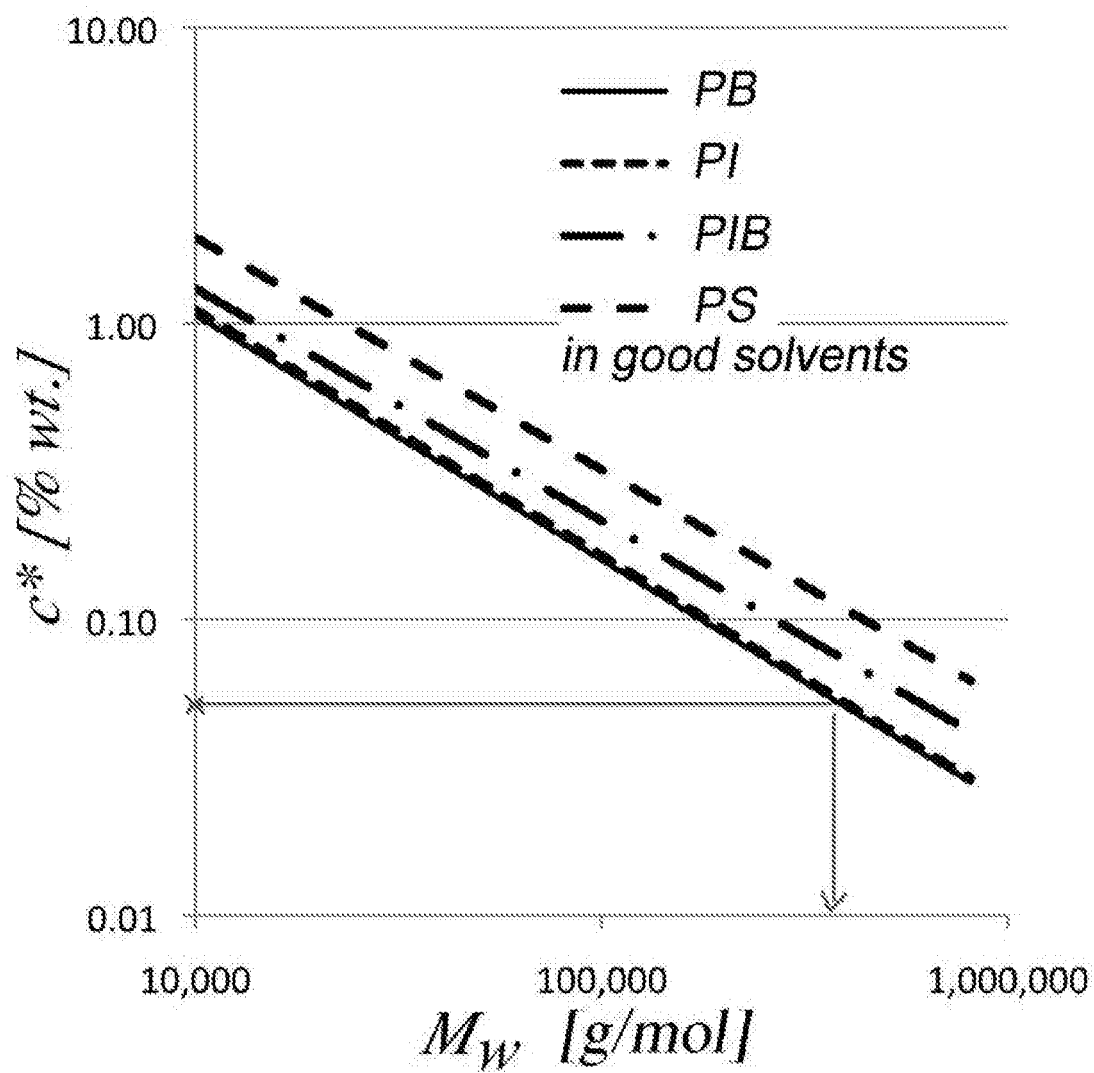
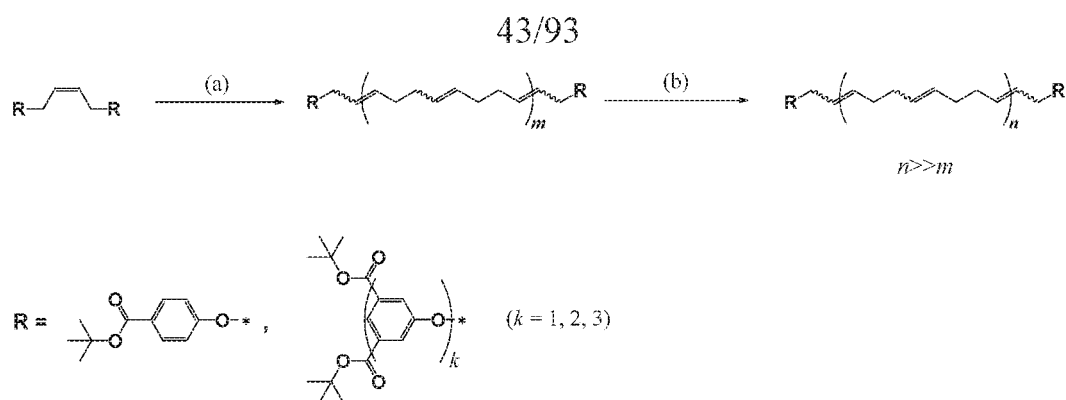
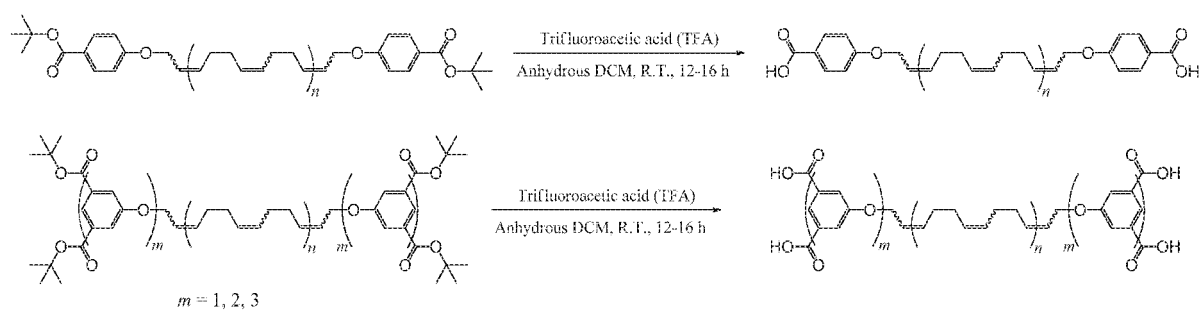
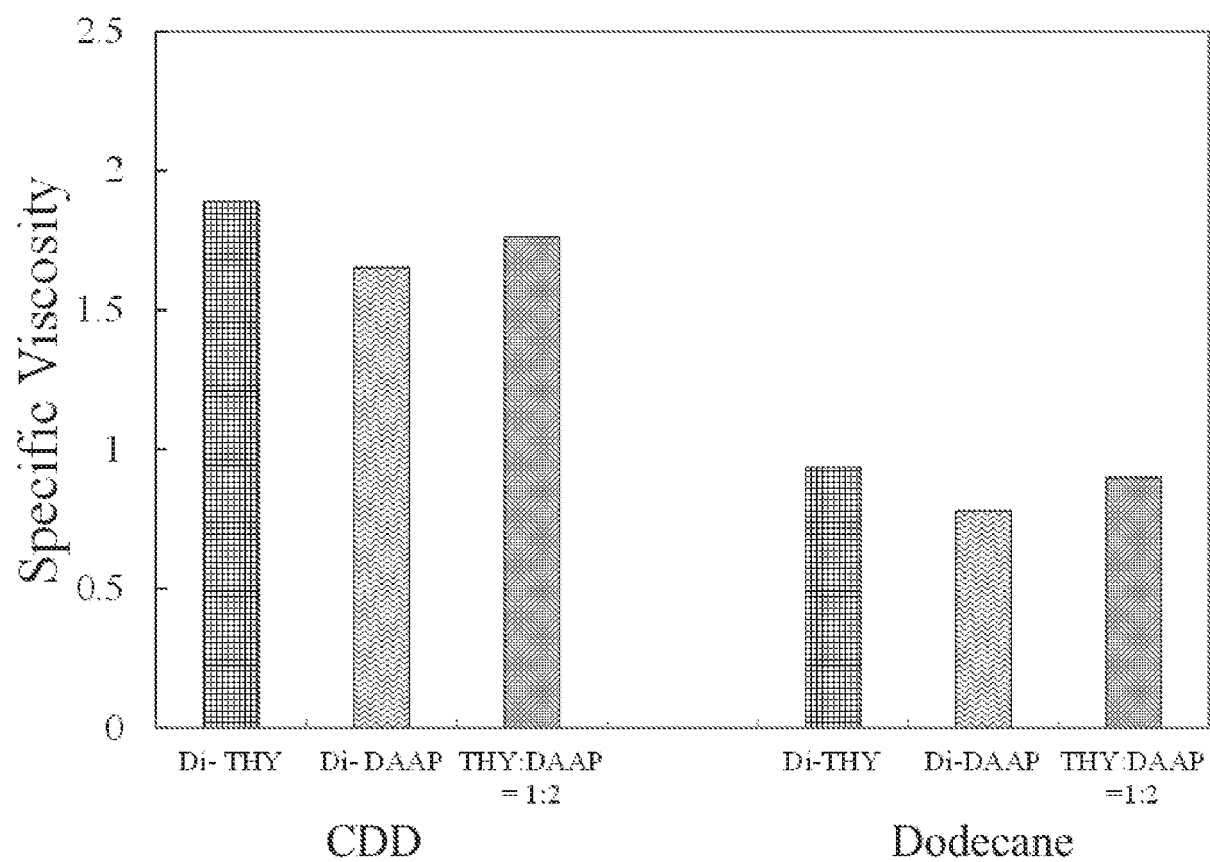


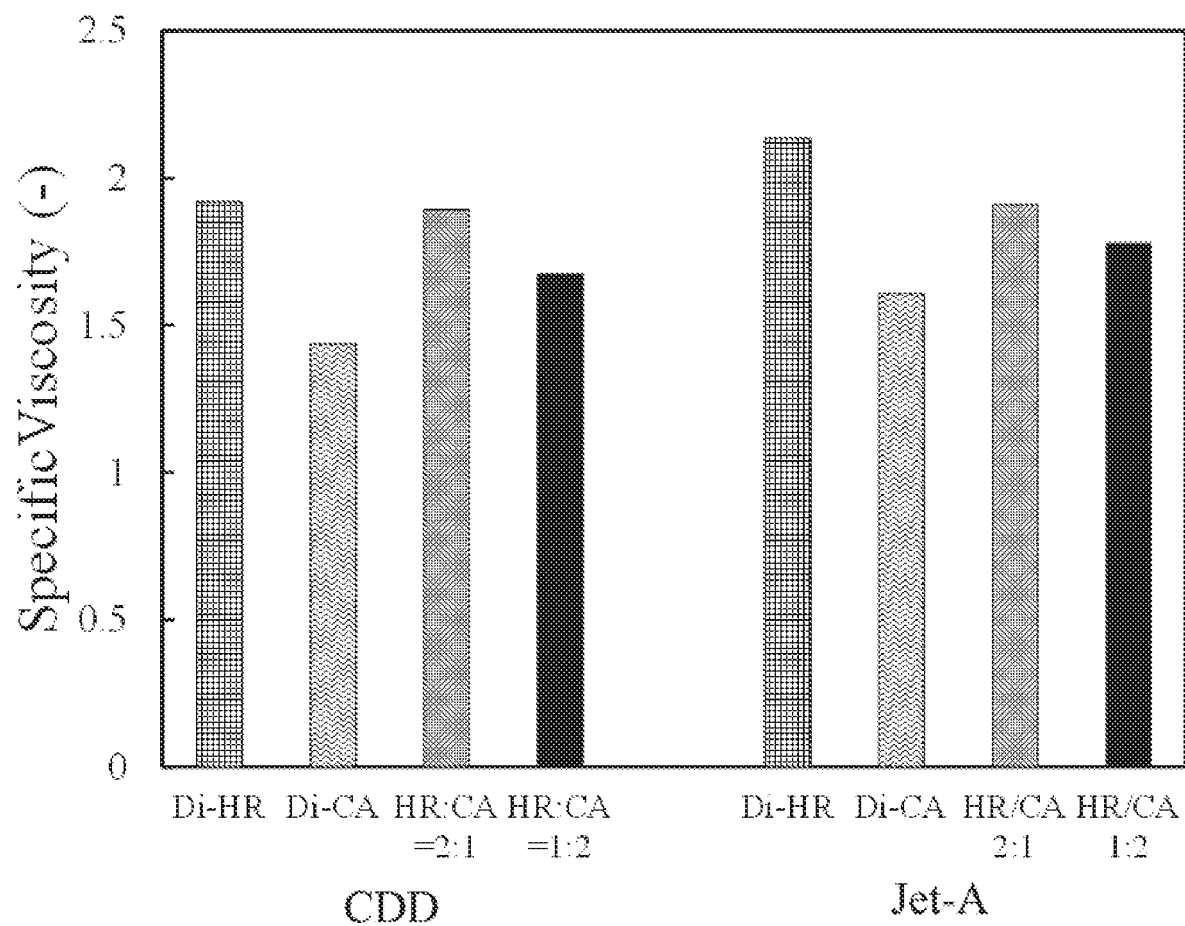
FIG. 40

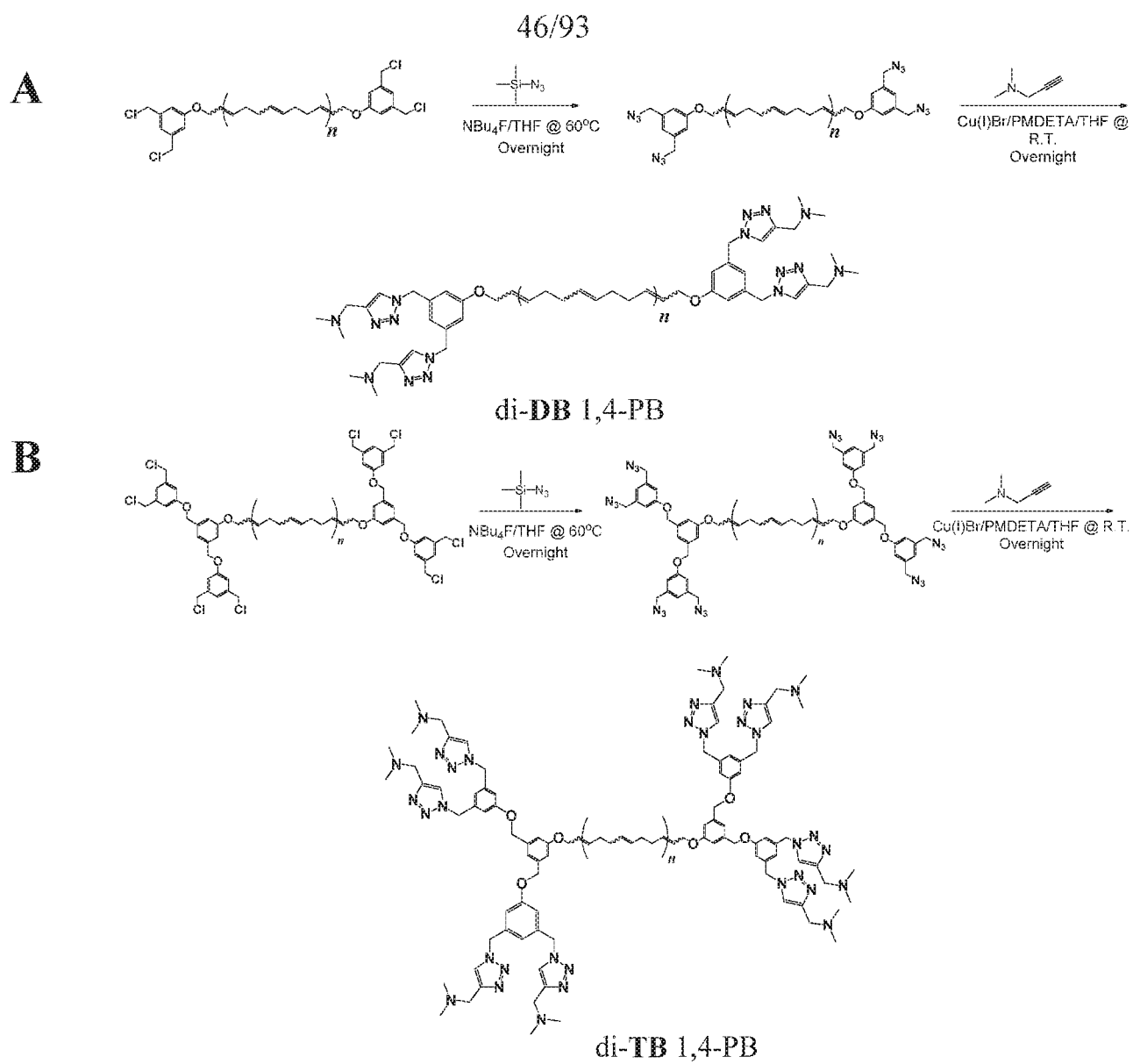
**FIG. 41****Figure 42**

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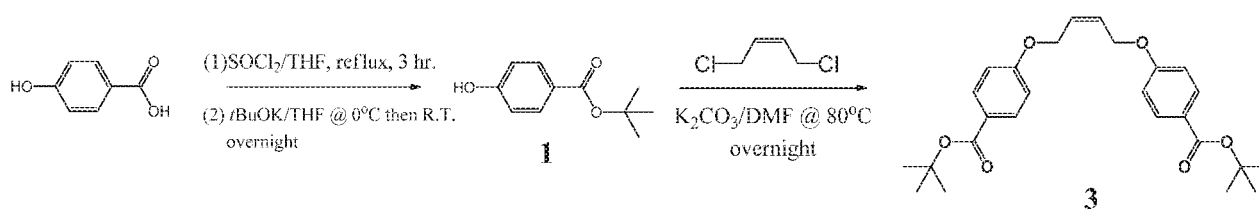
**FIG. 43**

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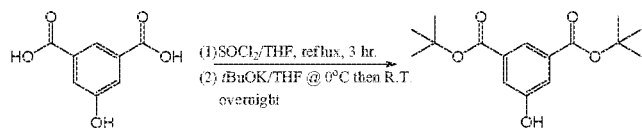
**FIG. 44**

**FIG. 45**

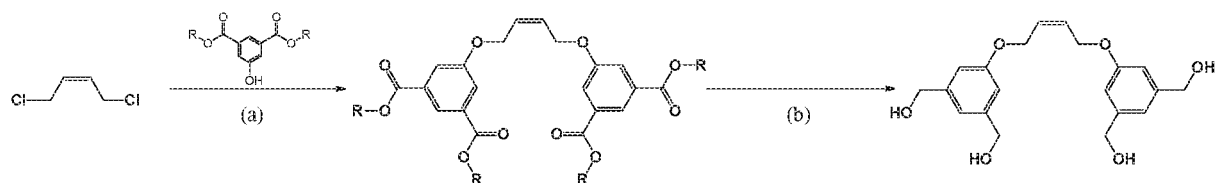
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**FIG. 46A**

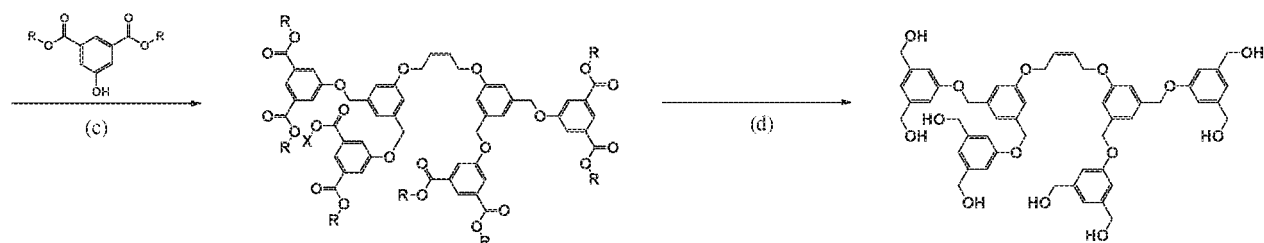
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2



6

4: $\text{R} = \text{CH}_3$ 5: $\text{R} = \text{C}(\text{CH}_3)_3$ 

9

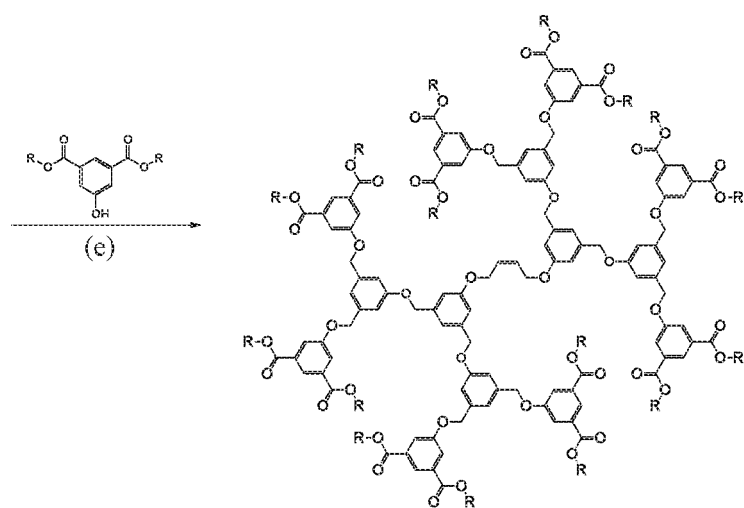
7: $\text{R} = \text{CH}_3$ 8: $\text{R} = \text{C}(\text{CH}_3)_3$ 10: $\text{R} = \text{C}(\text{CH}_3)_3$

FIG. 46B

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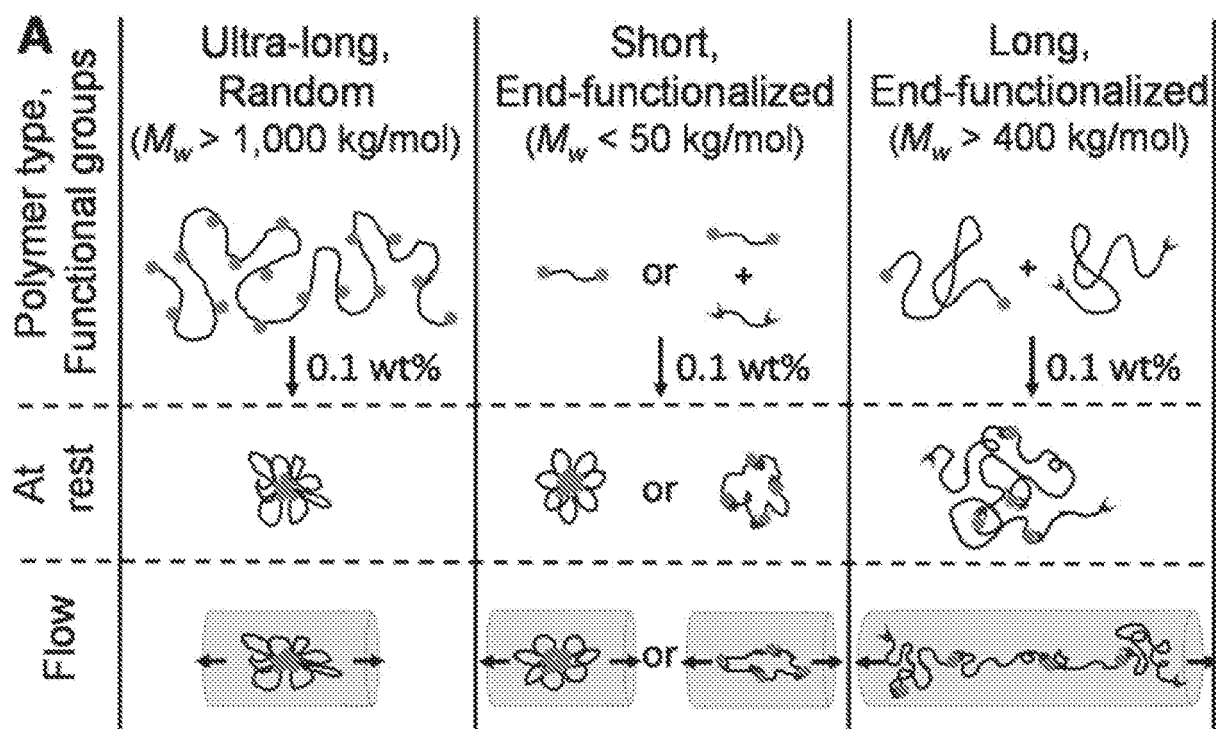


FIG. 47A

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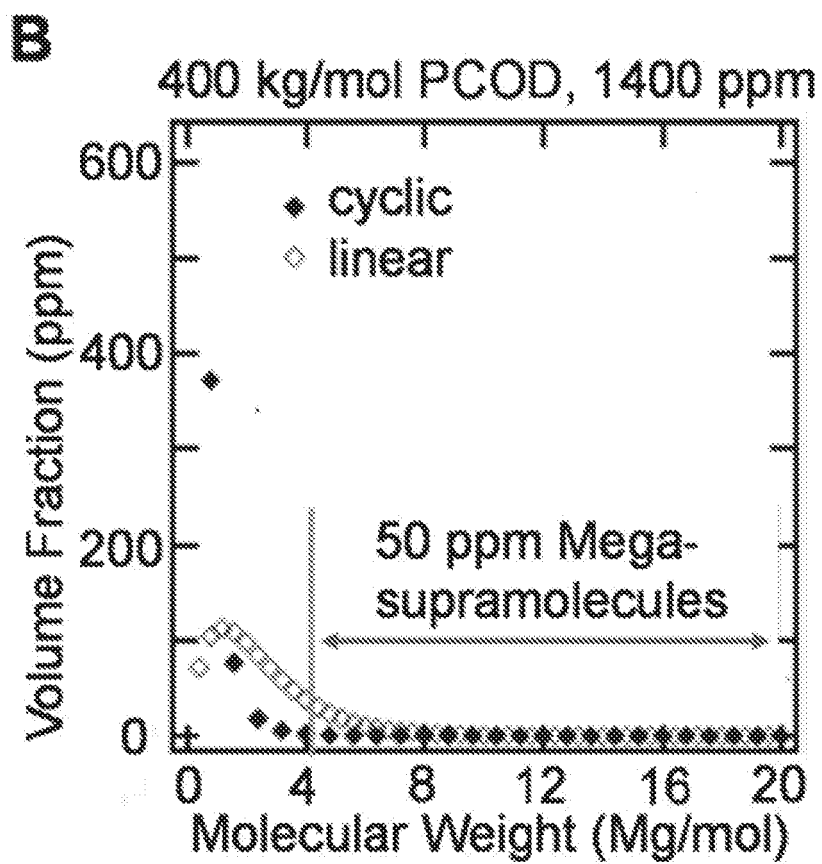


FIG. 47B

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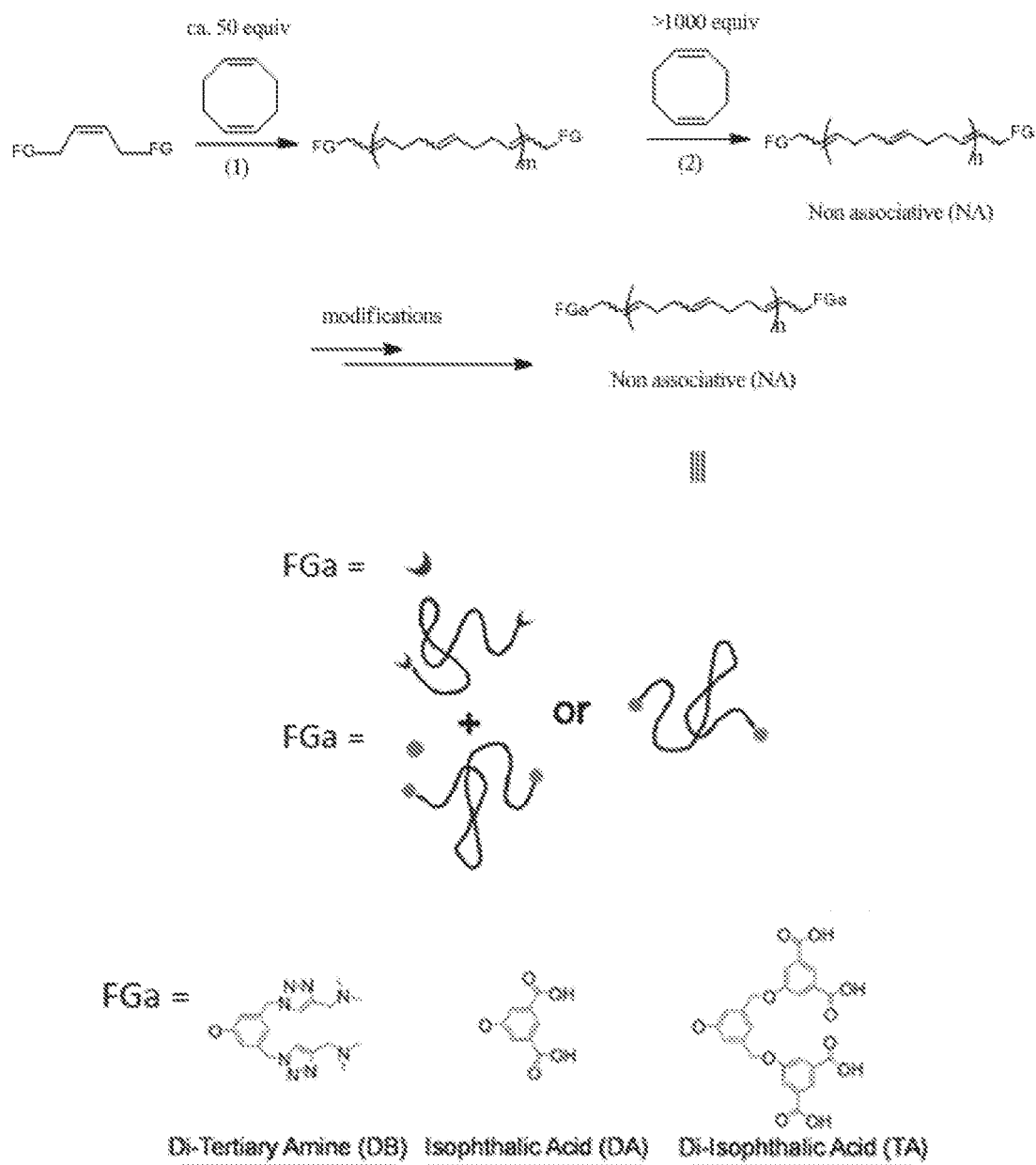


FIG. 47C

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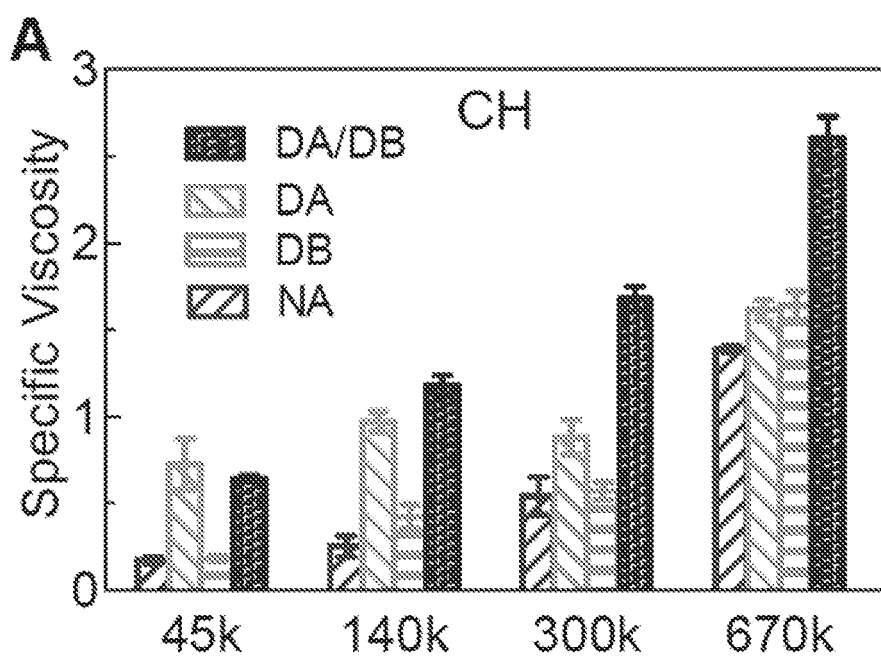


FIG. 48A

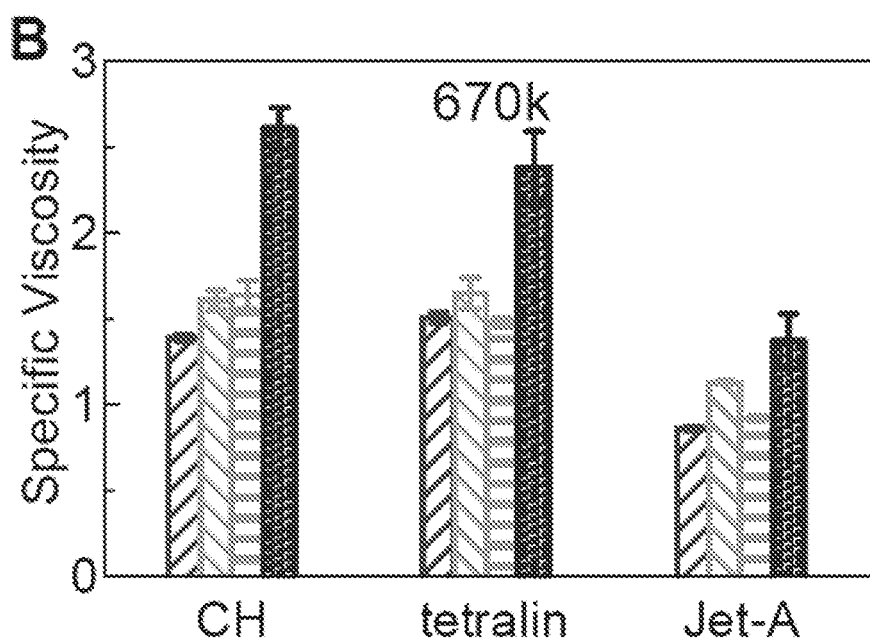


FIG. 48B

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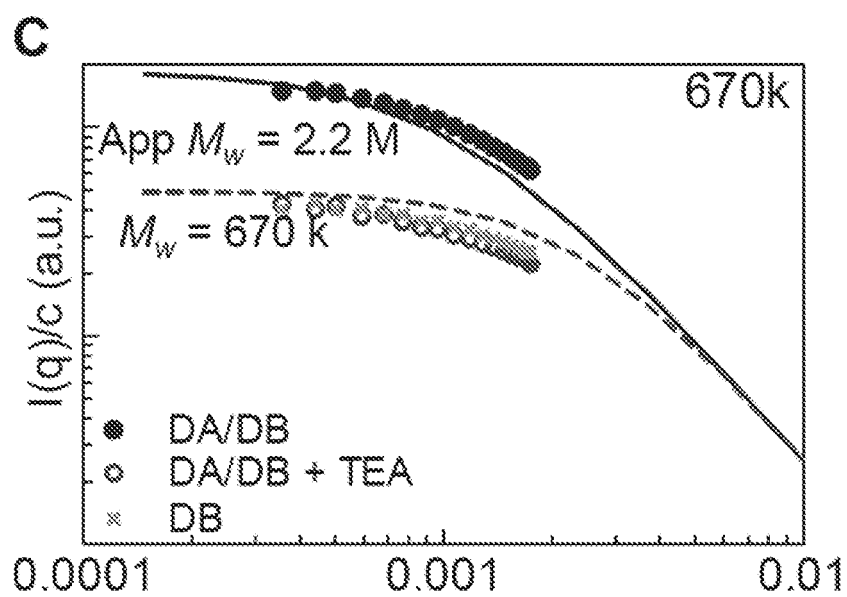


FIG. 48C

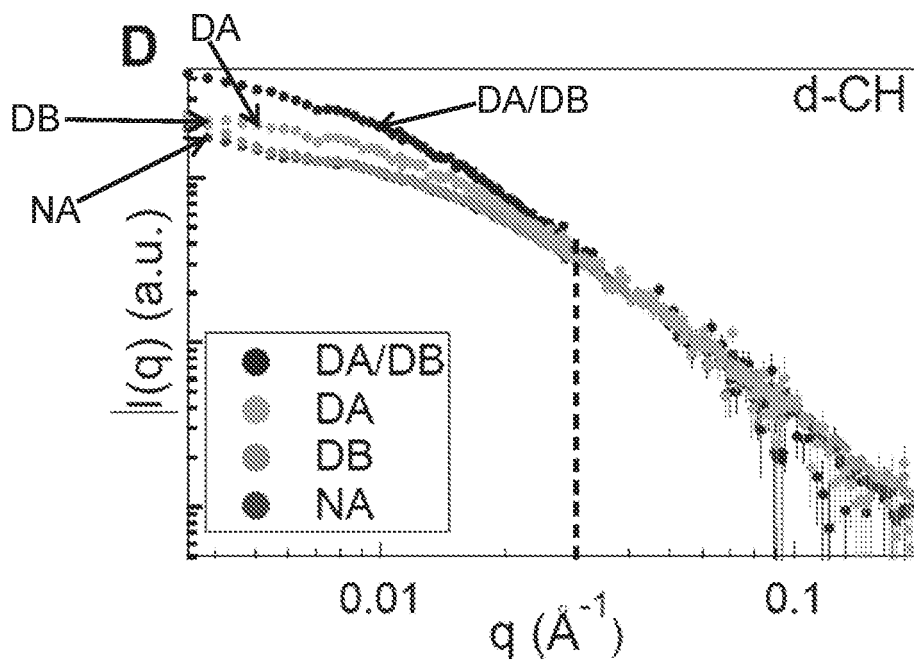


FIG. 48D

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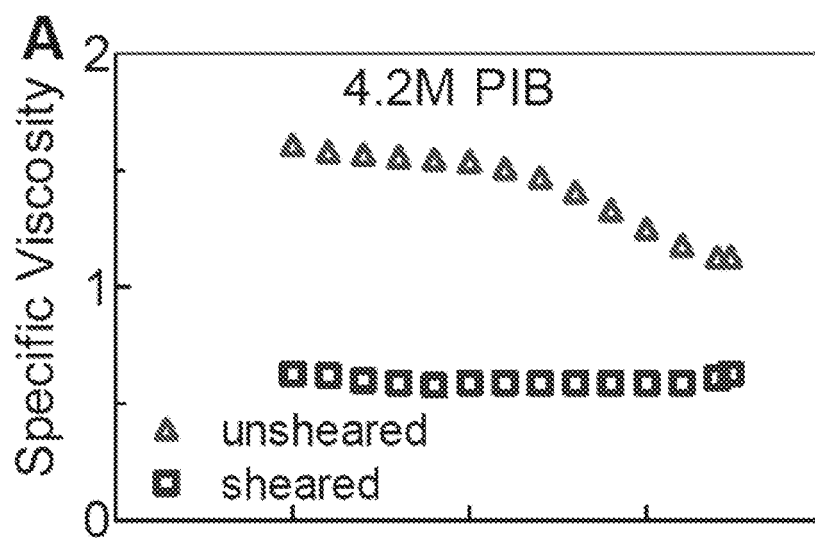


FIG. 49A

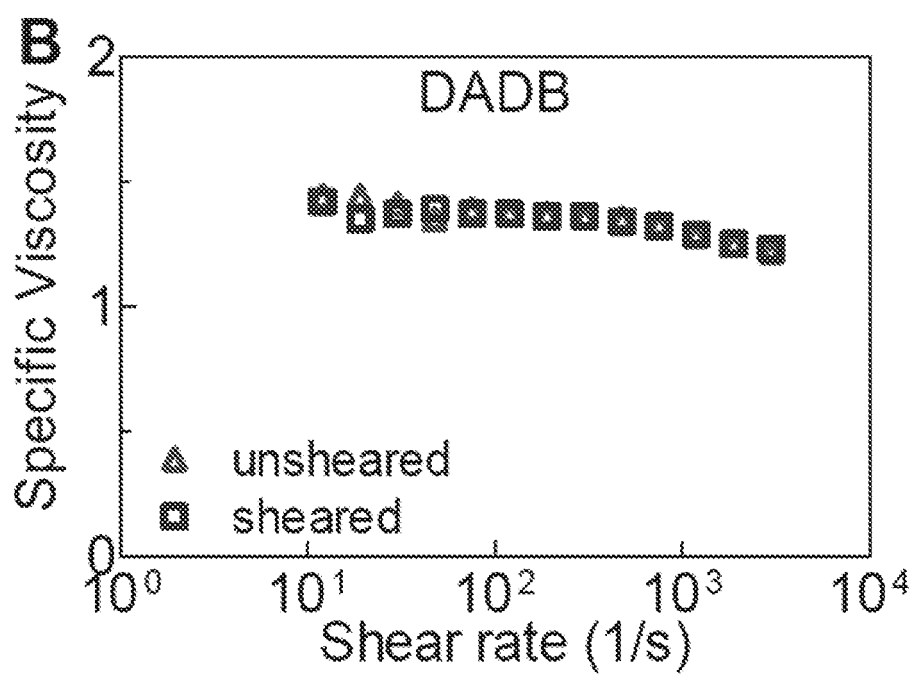
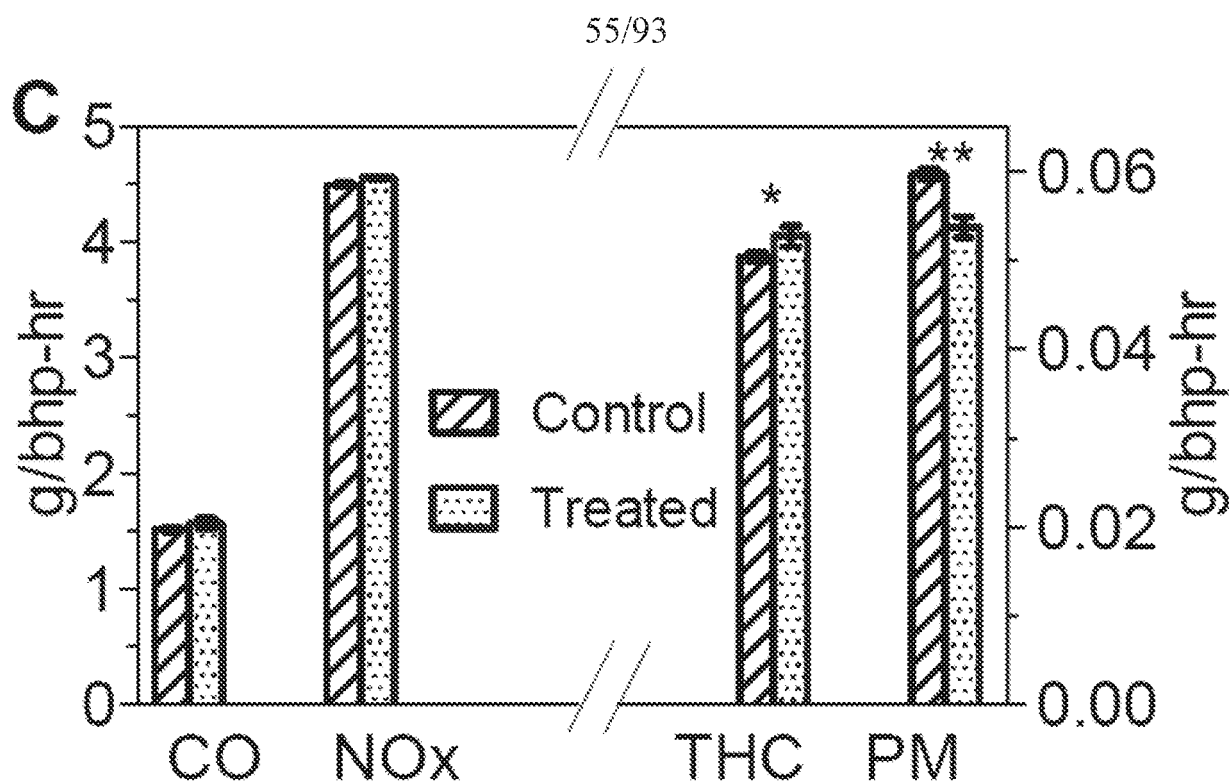


FIG. 49B



* : $p = 0.035$

** : $p = 0.002$

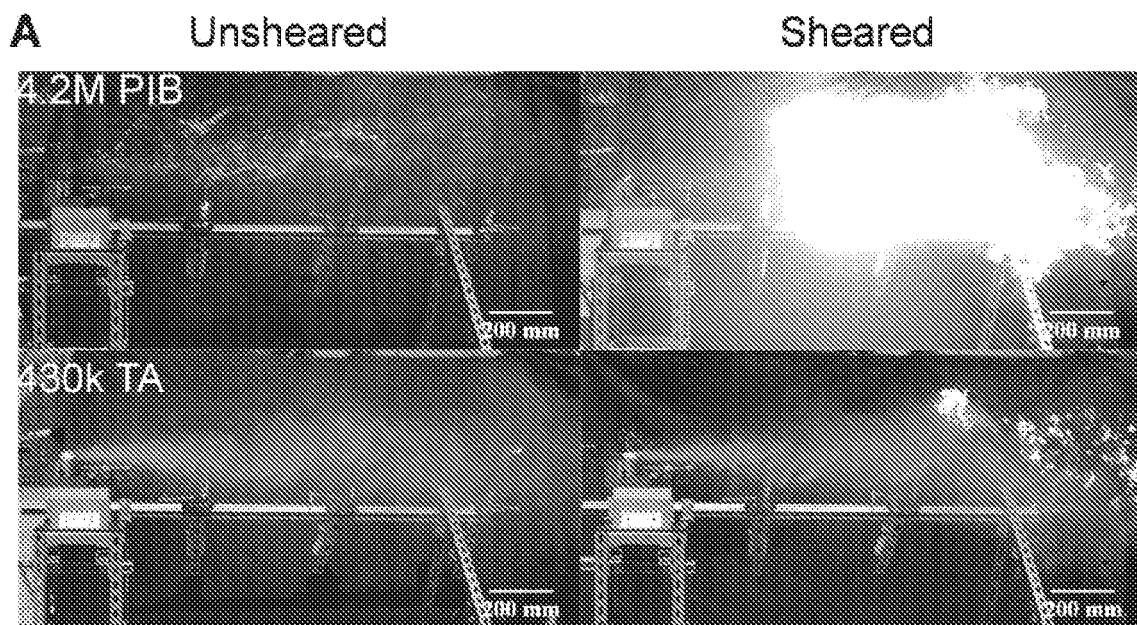
THC = Total Hydrocarbon

PM = Particulate Matter

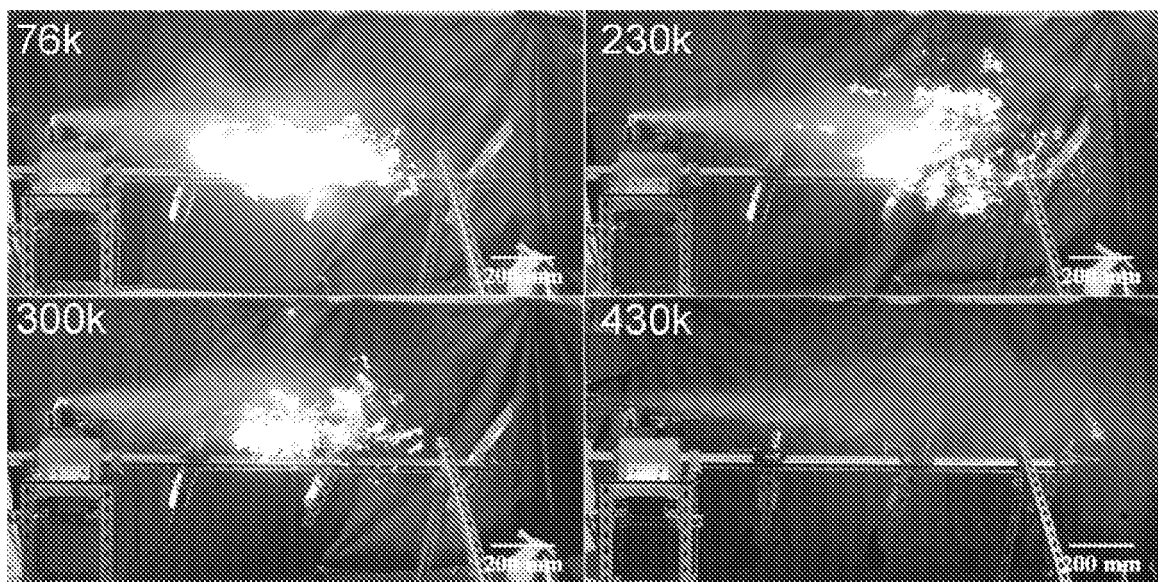
Bhp-hr = brake-horsepower-hr
= 0.746 kW·hr

FIG. 49C

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**FIG. 50A**

B All solutions below are unsheared

**FIG. 50B**

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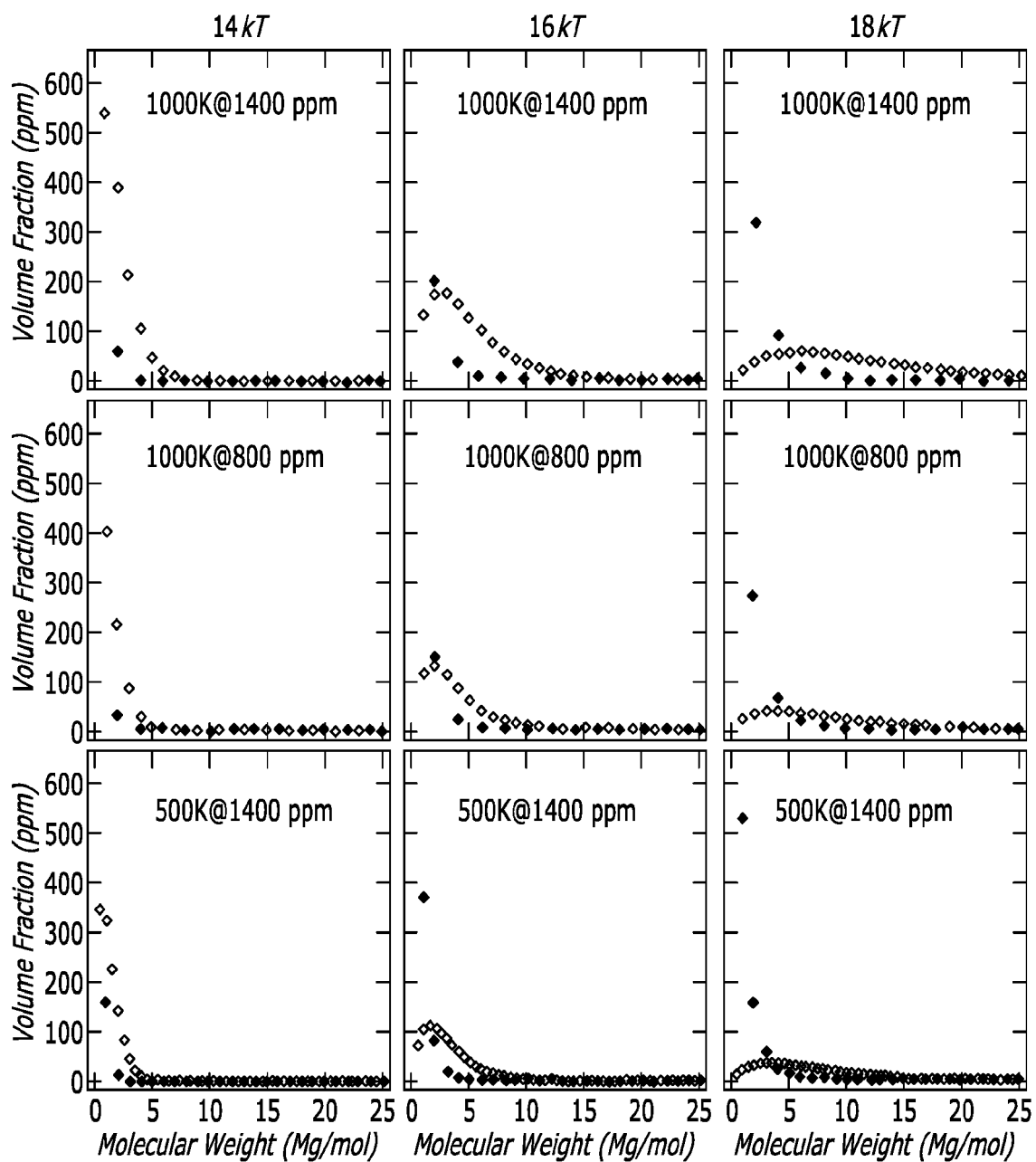


FIG. 51

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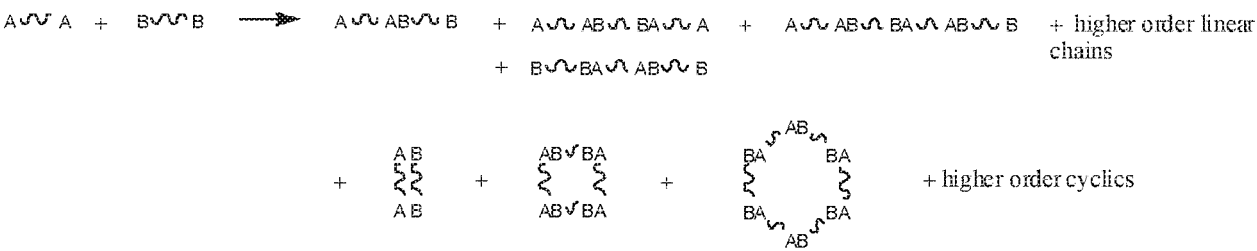
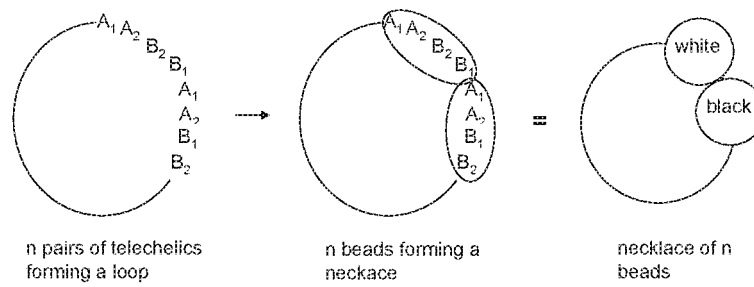
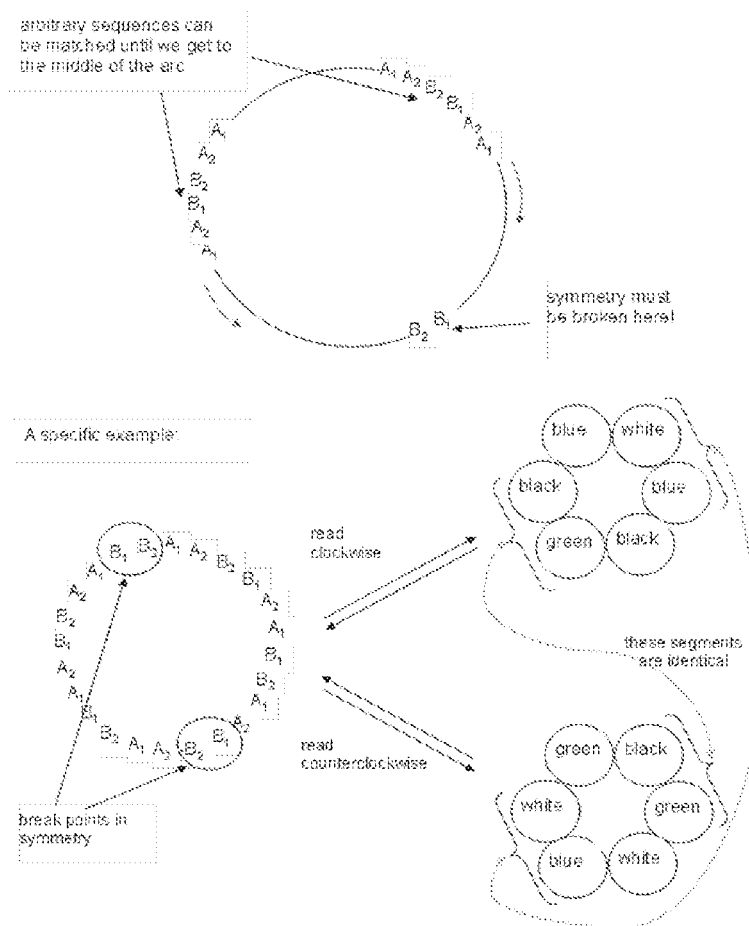


FIG. 52

Polymer components:	Group index g :	Degeneracy Ω_g :
$A \text{-----} A$	1	1
$B \text{-----} B$	2	1
$A \text{-----} A \text{-----} B \text{-----} B$	3	4
$\begin{matrix} AB \\ \text{---} \end{matrix}$	4	2
$A \text{-----} A \text{-----} B \text{-----} BA \text{-----} A$	5	4
$B \text{-----} B \text{-----} A \text{-----} AB \text{-----} B$	6	4
$A \text{-----} A \text{-----} B \text{-----} BA \text{-----} AB \text{-----} B$	7	16
$\begin{matrix} AB \\ \text{---} \\ A \text{-----} B \\ \text{---} \\ B \text{-----} A \end{matrix}$	8	5
{Etc.}		

FIG. 53

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**FIG. 54****FIG. 55**

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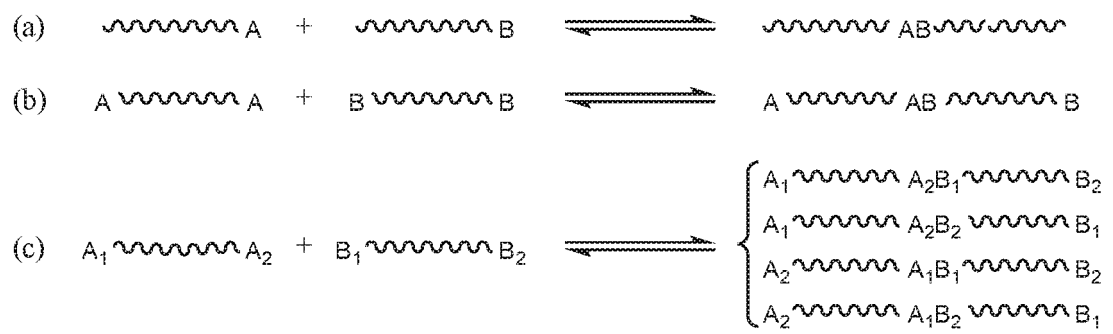


FIG. 56

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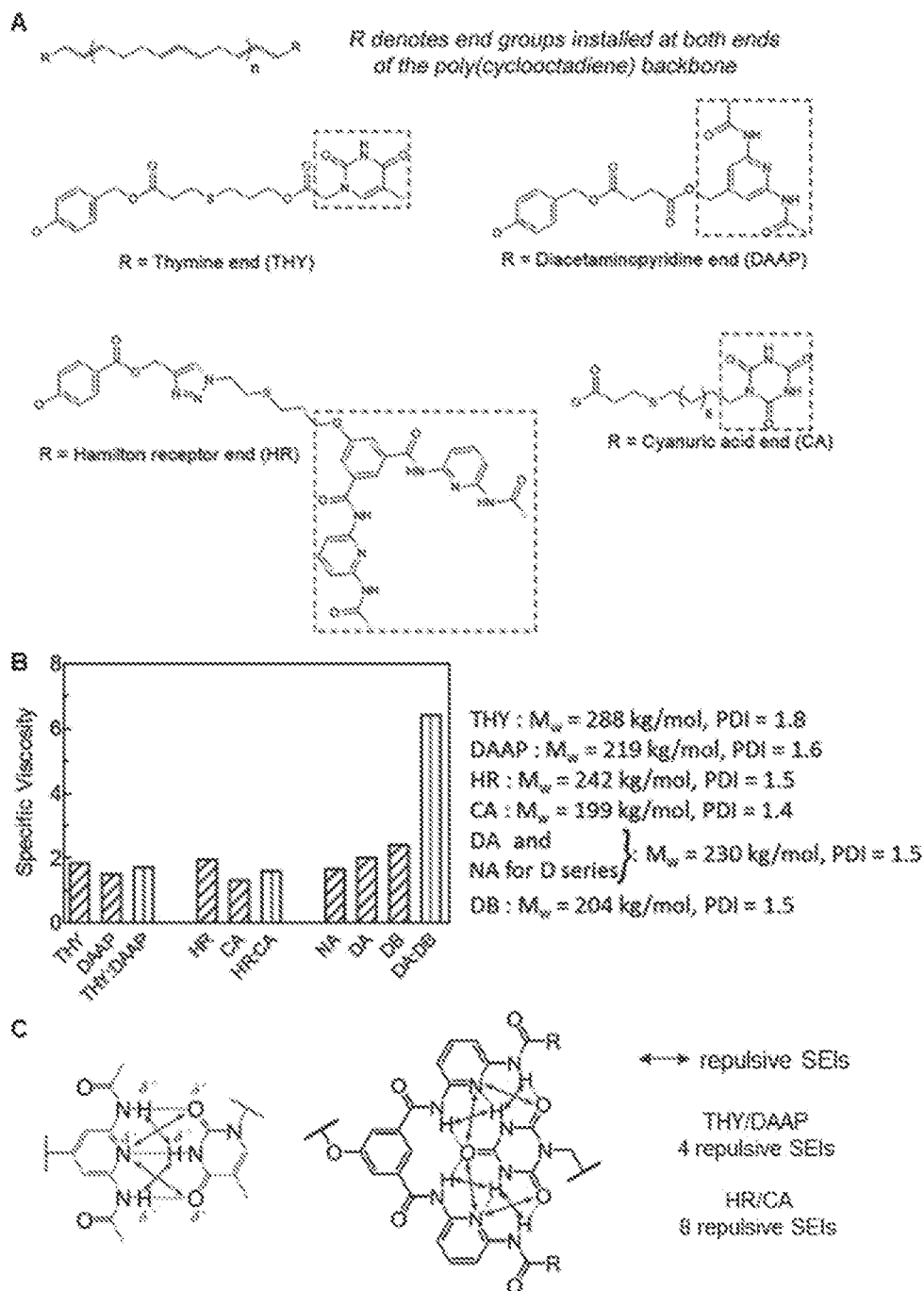


FIG. 57

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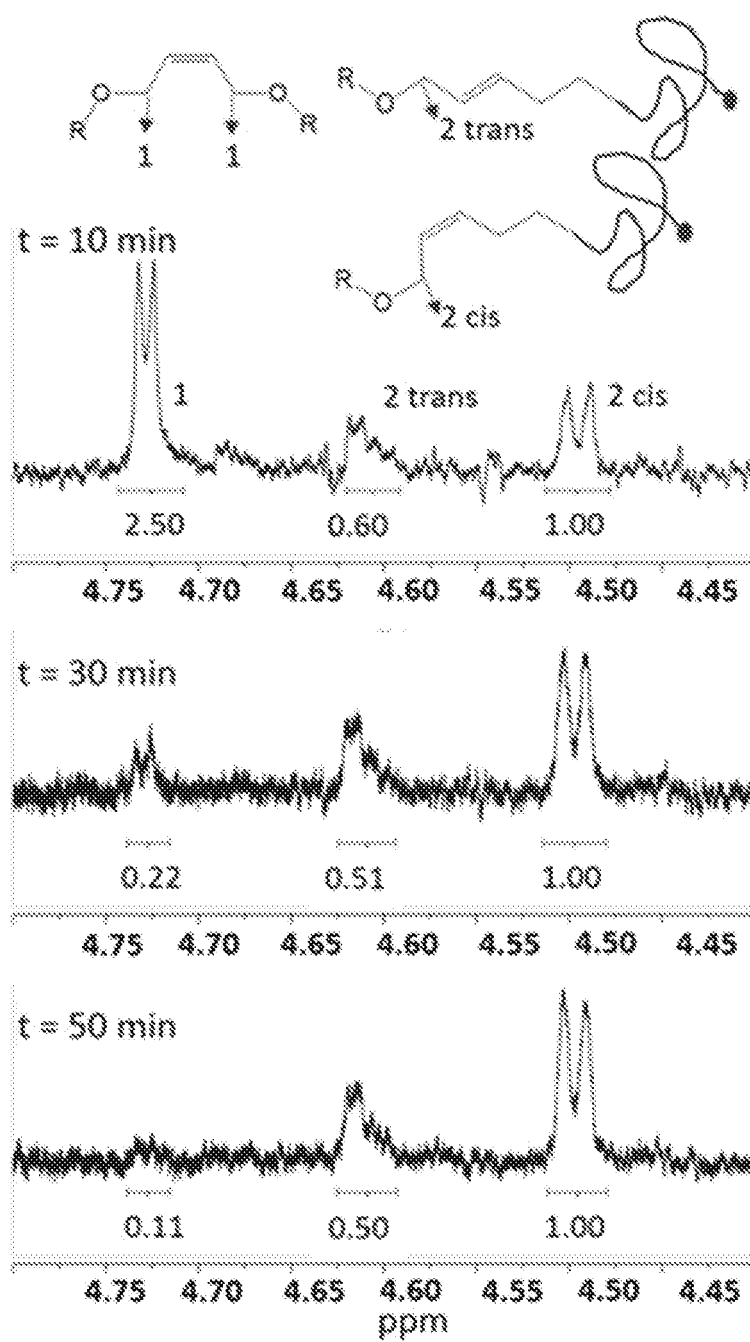


FIG. 58

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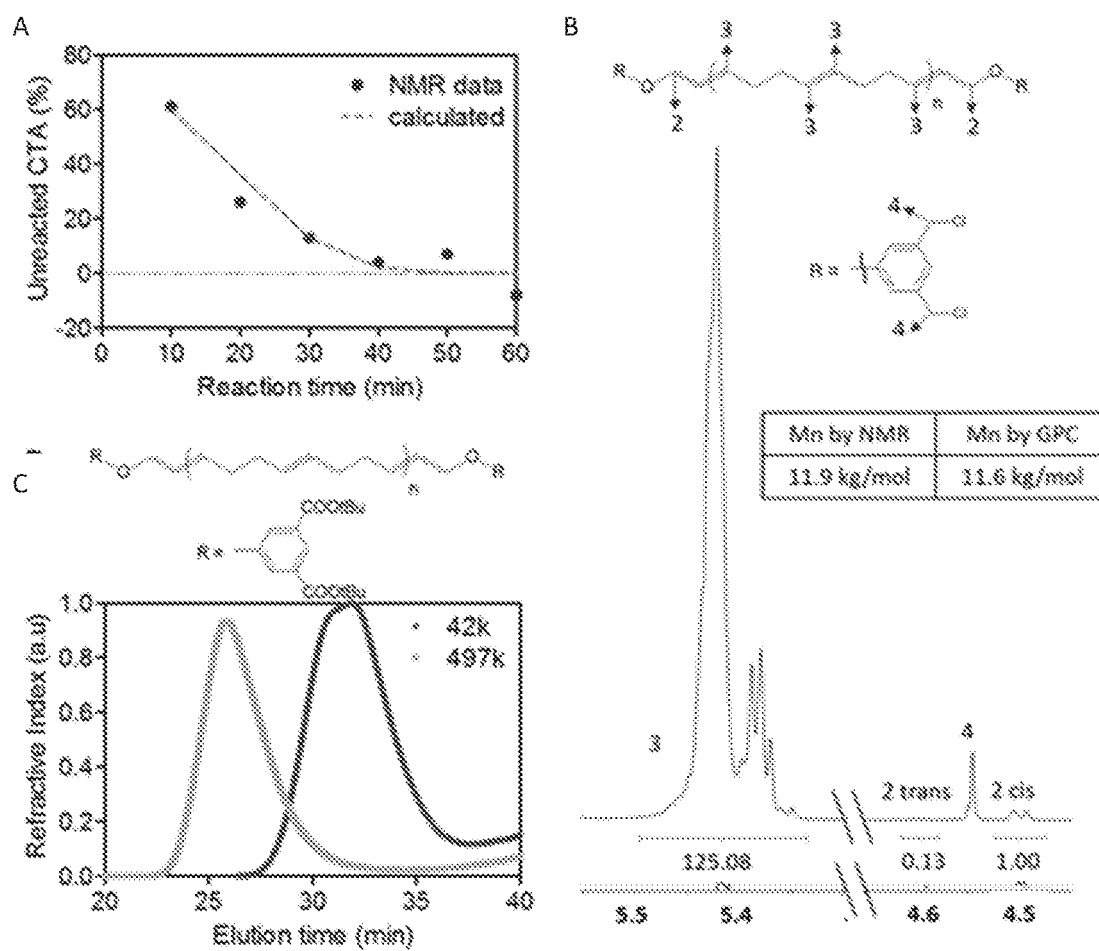


FIG. 59

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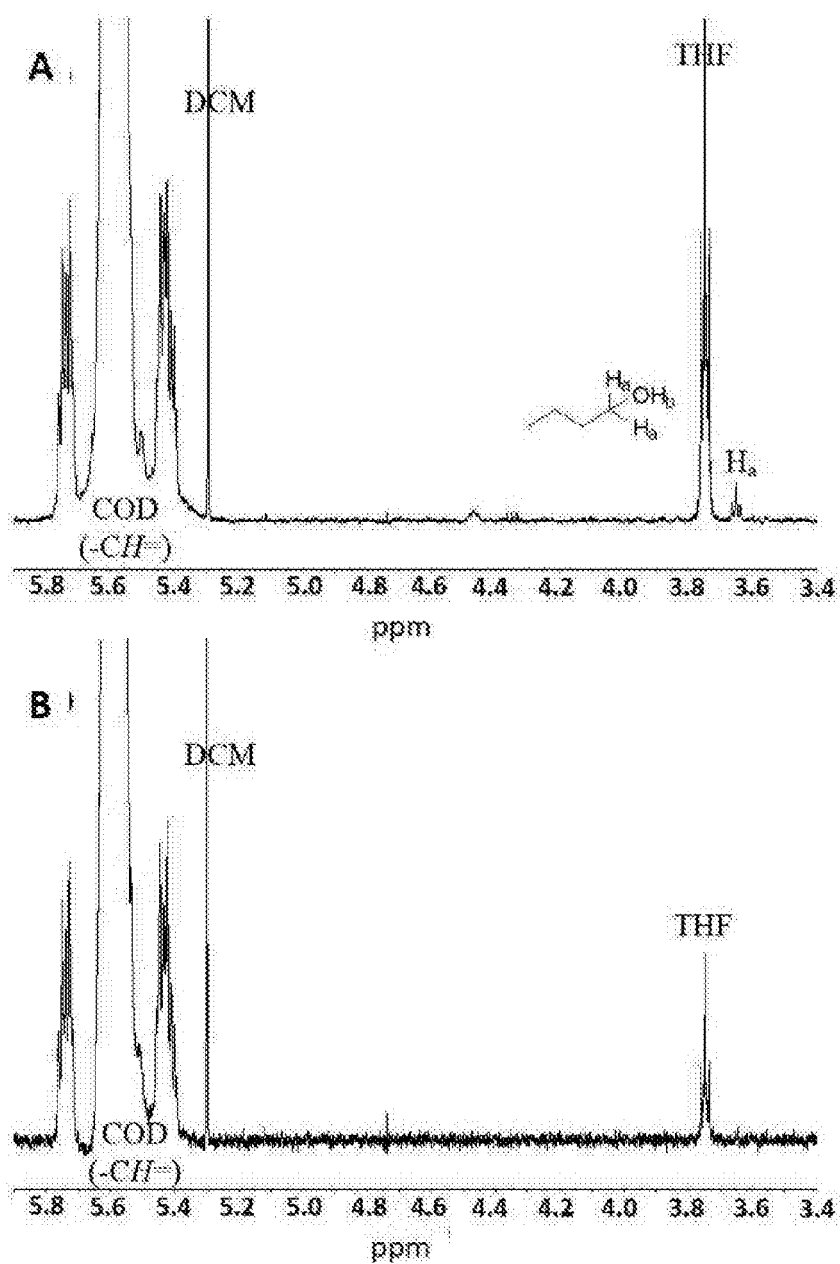
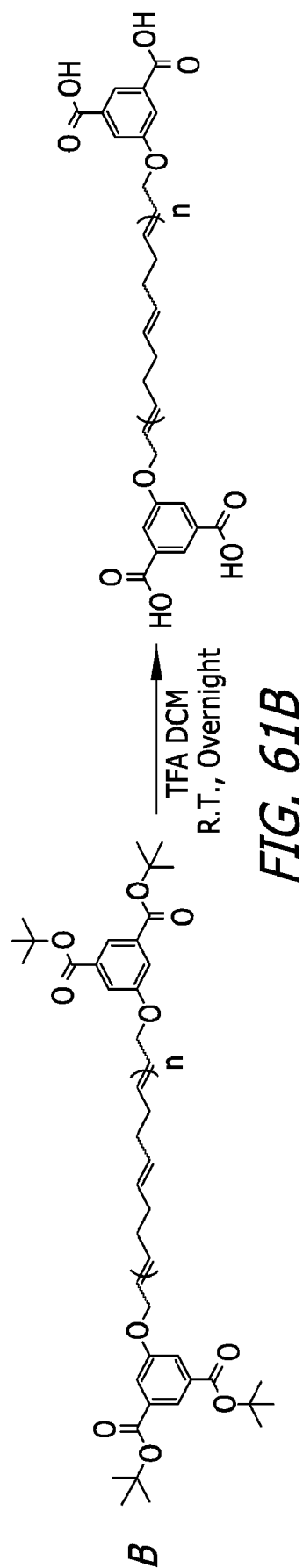
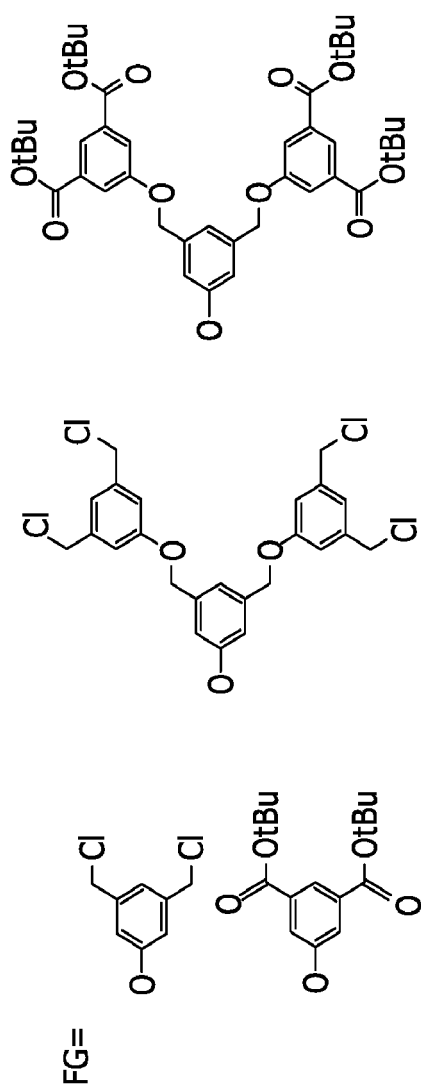
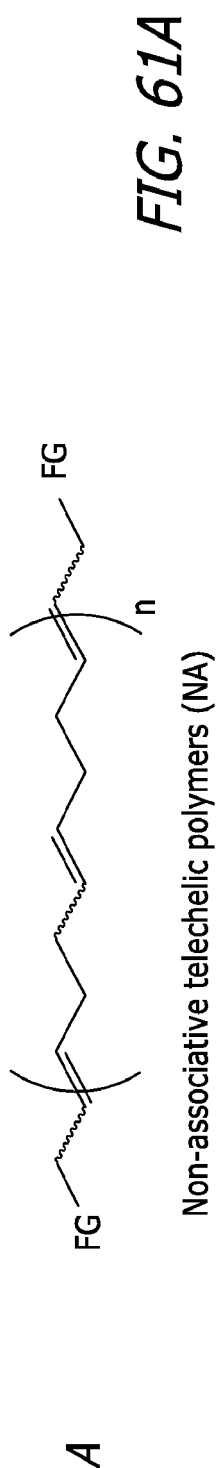


FIG. 60



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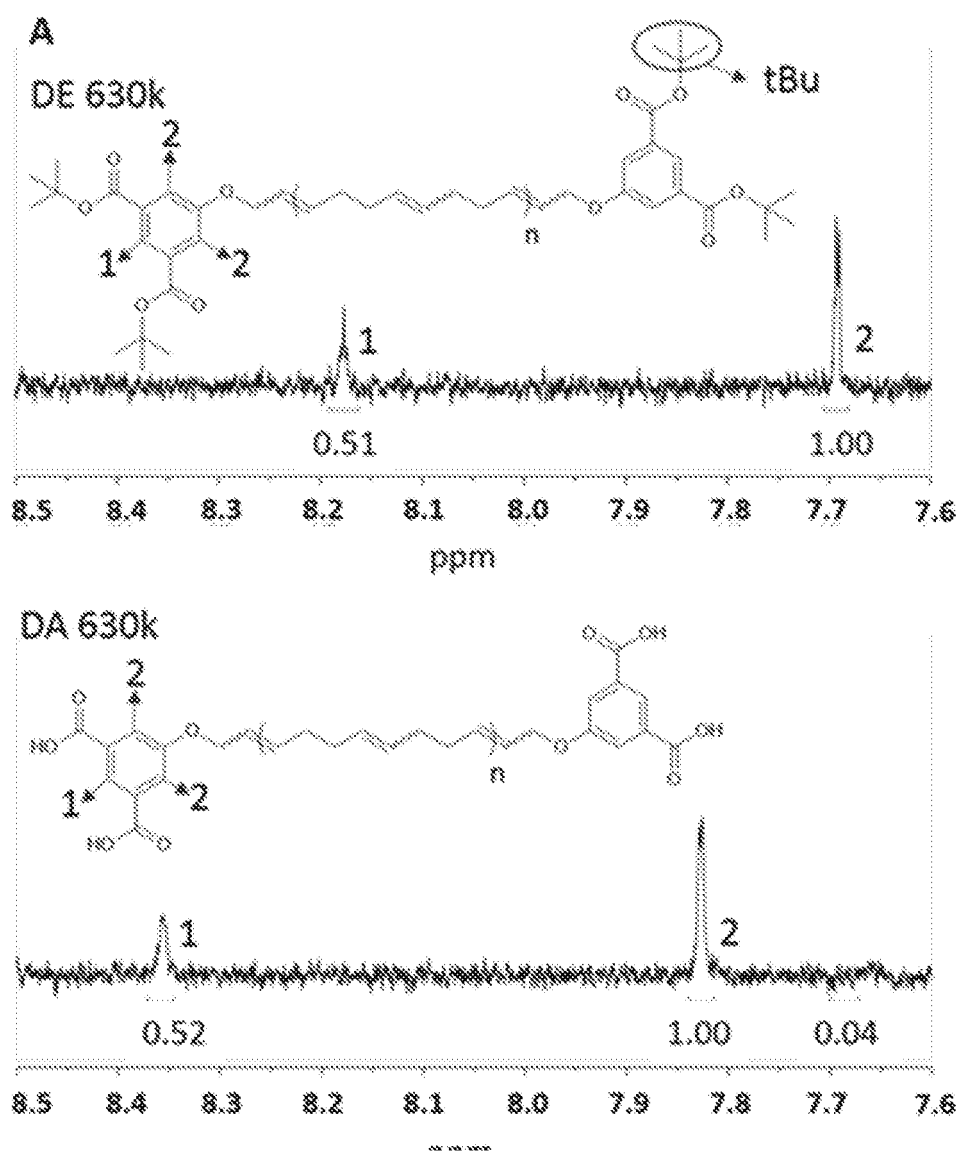


FIG. 62A

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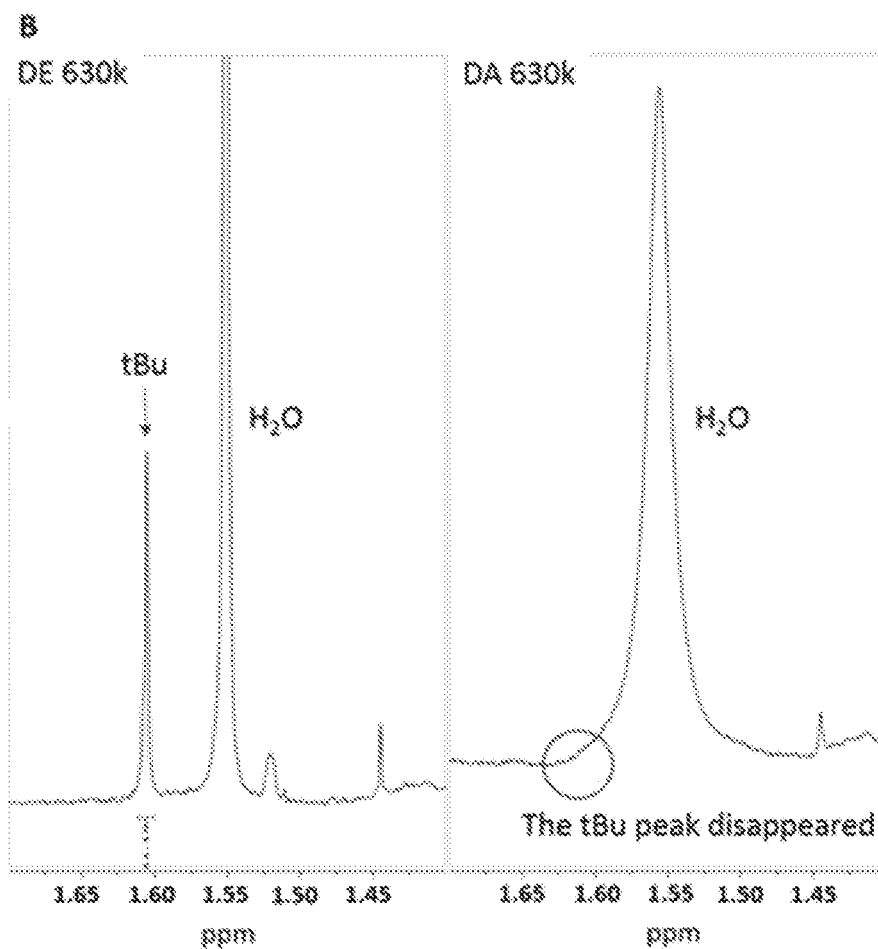


FIG. 62B

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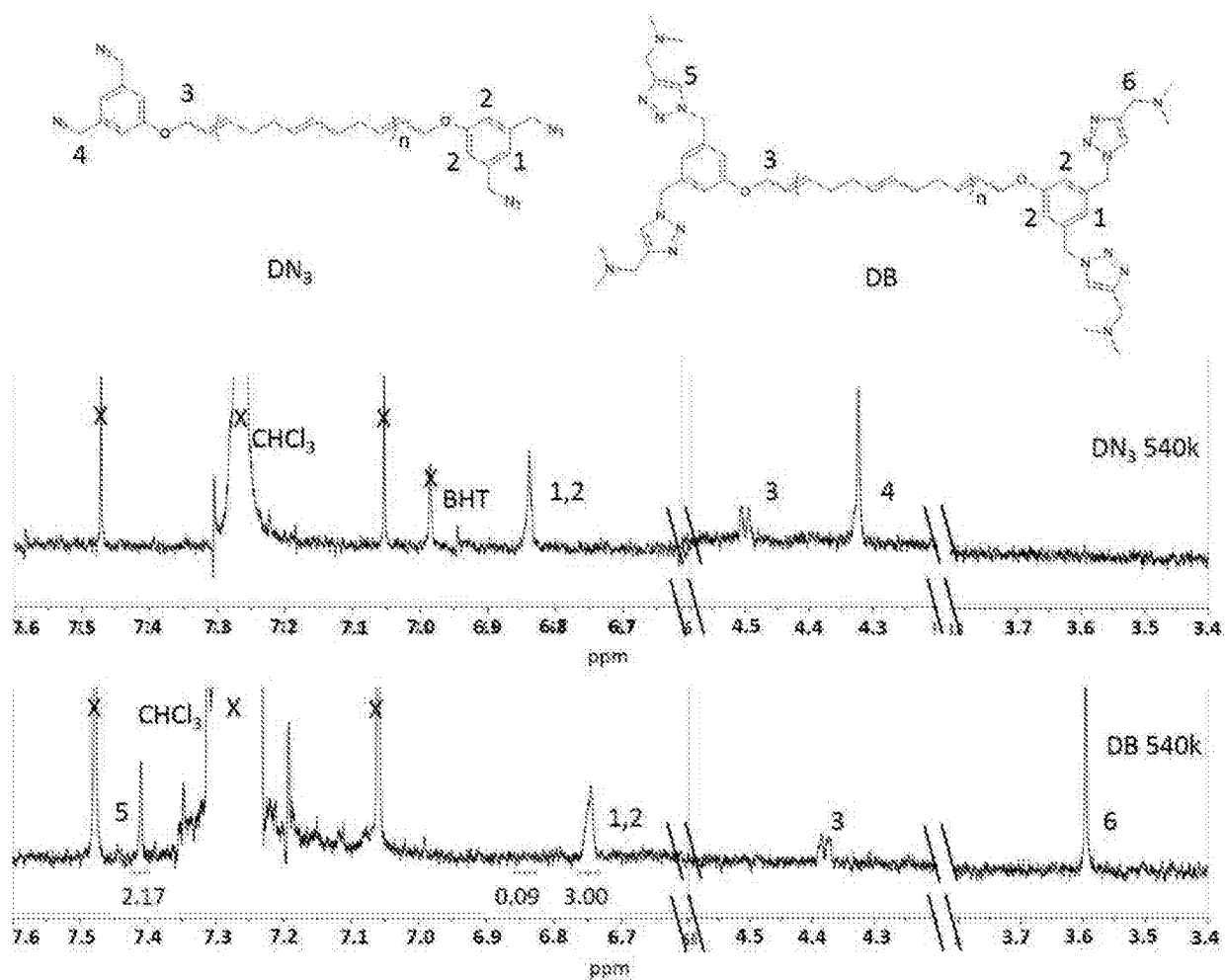
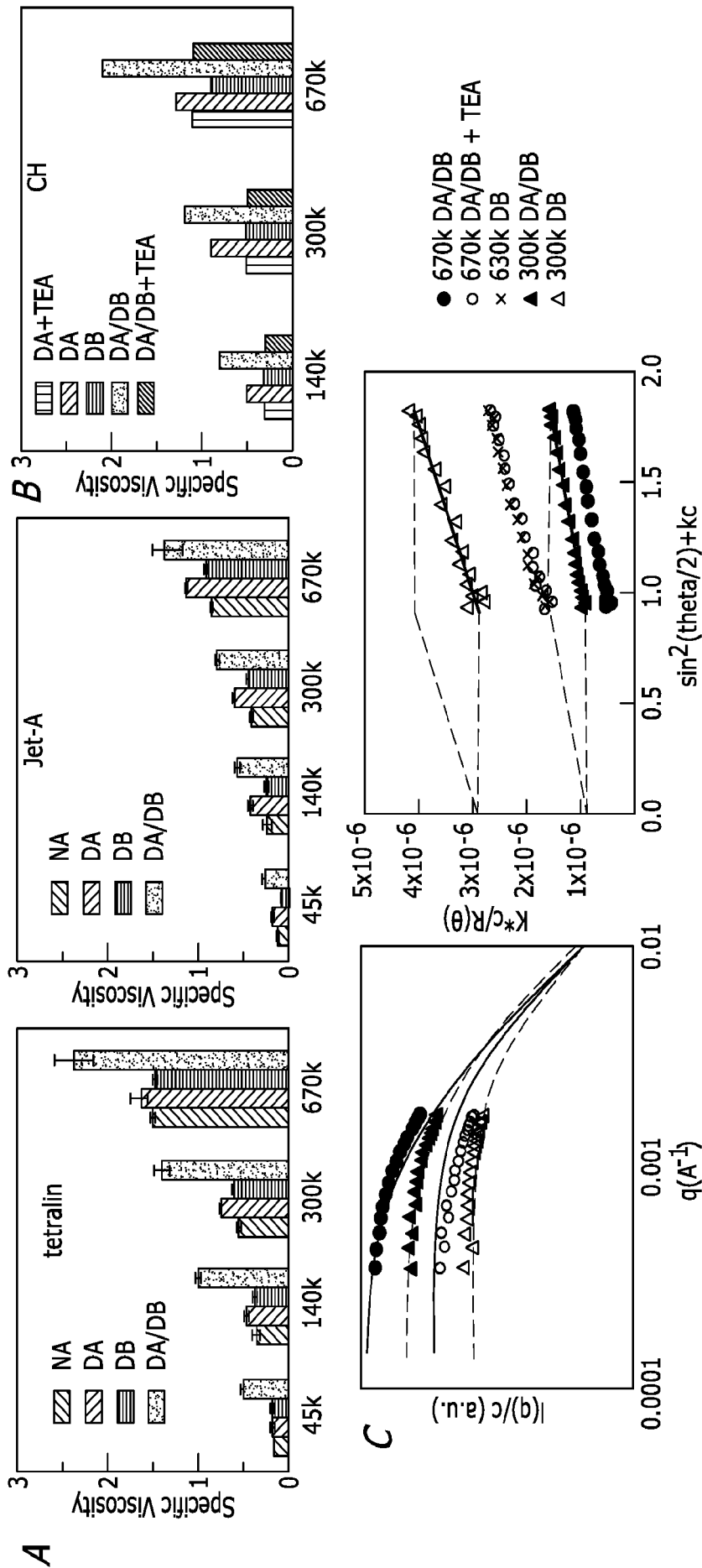


FIG. 62C

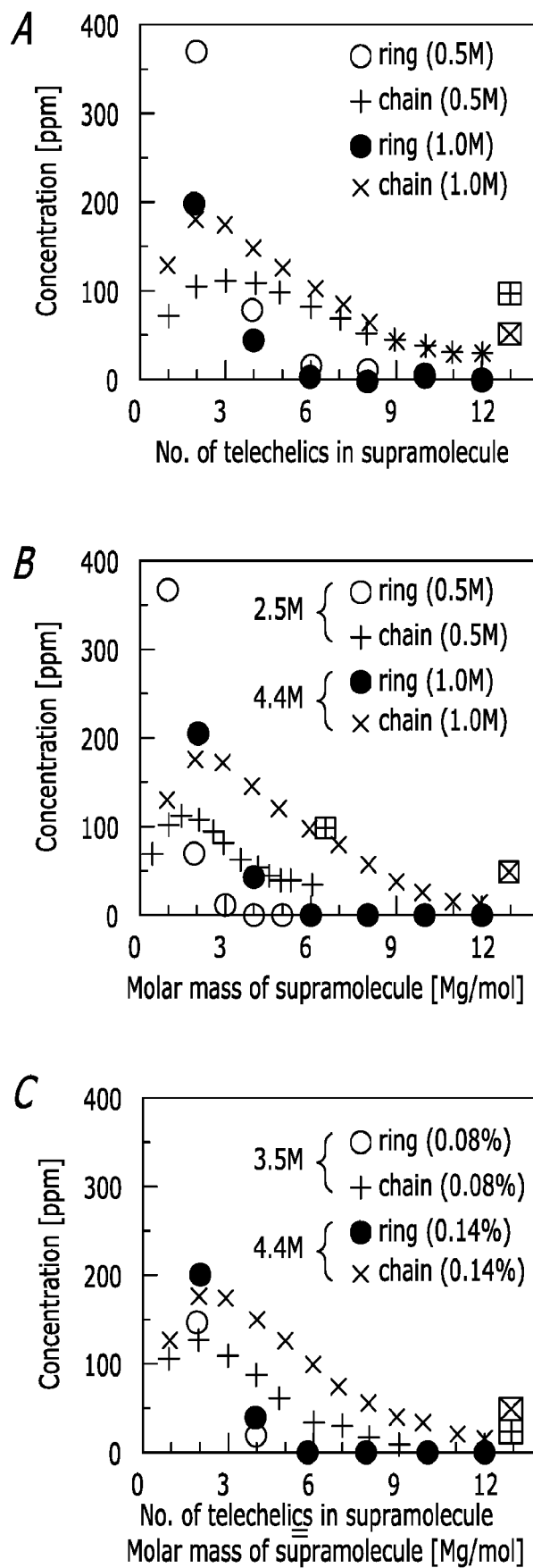


D

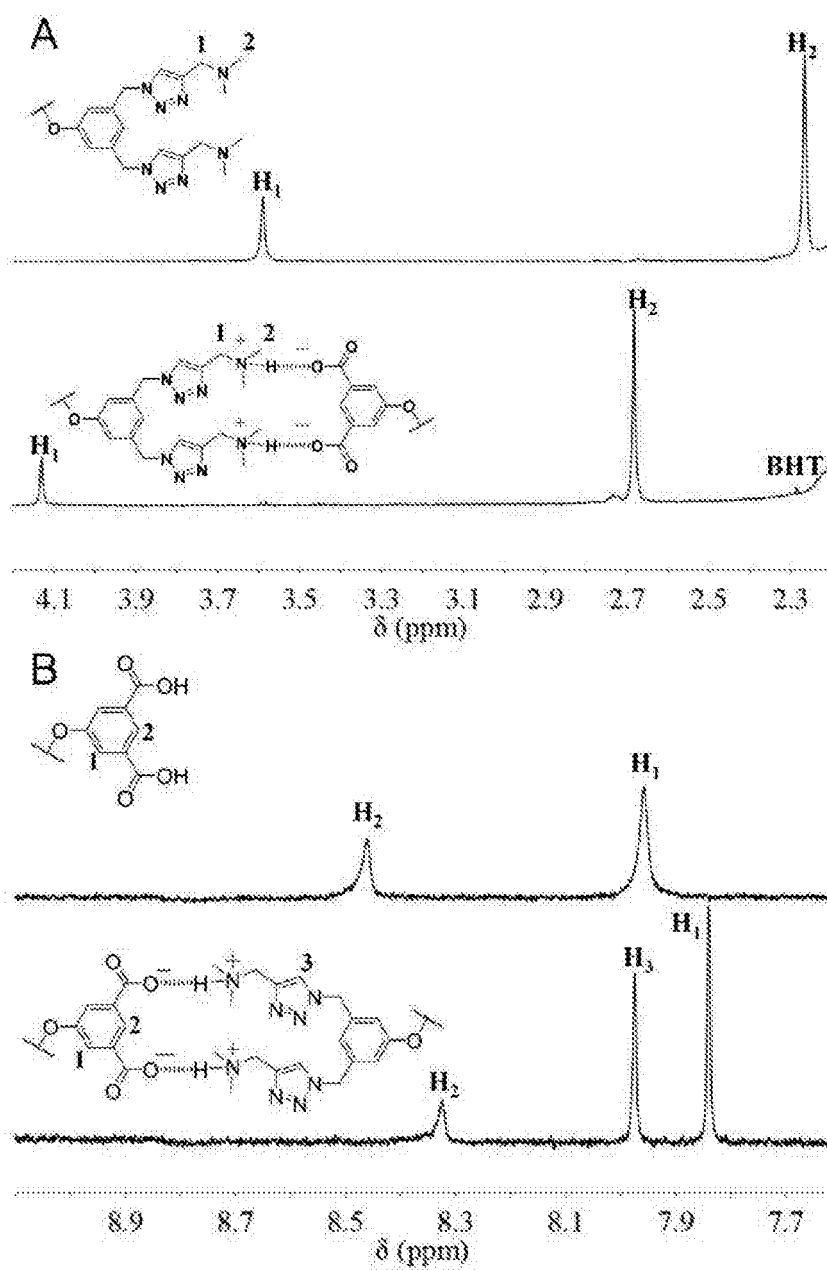
Associated		Not Associated	
		DA/DB+TEA	DB
670k DA/DB	app Mw	(2.2±0.2) e+6 g/mol	(6.1±0.5) e+5 g/mol
	app Rg	87±4 nm	58±3 nm
300k DA/DB	app Mw	(1.1±0.4) e+6 g/mol	(3.2±0.3) e+5 g/mol
	app Rg	60±3 nm	36±6 nm

FIG. 63

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**FIG. 64**

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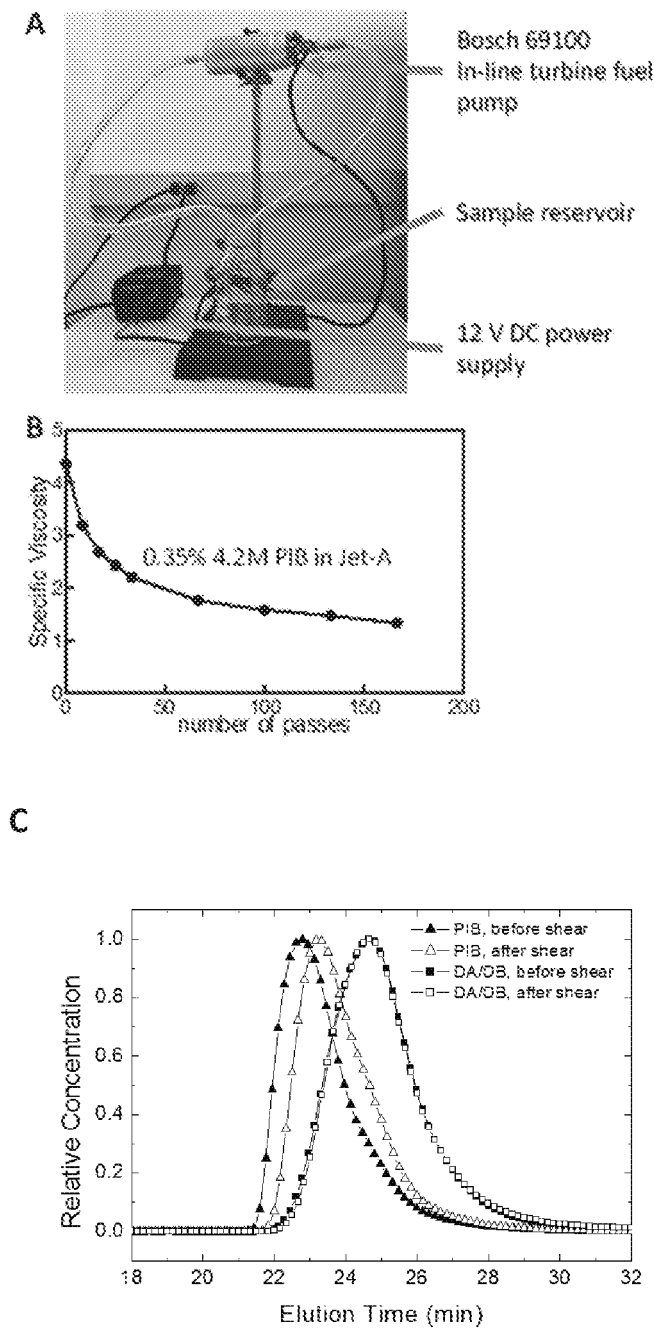


FIG. 66

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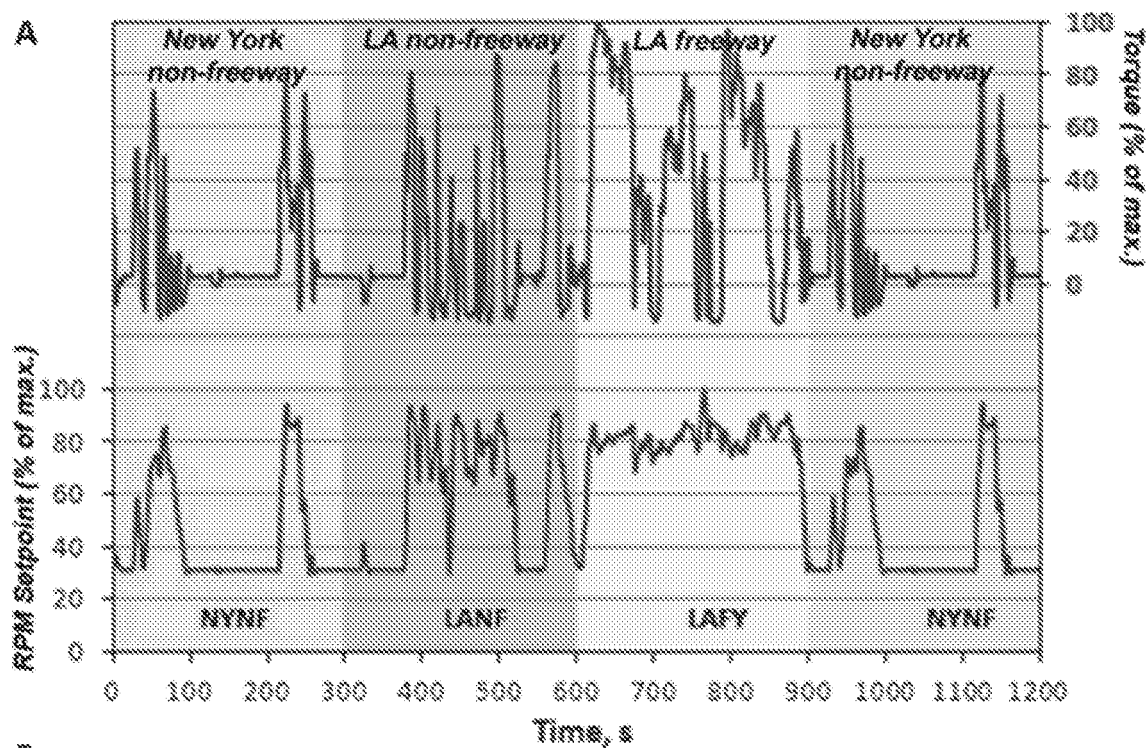


FIG. 67A

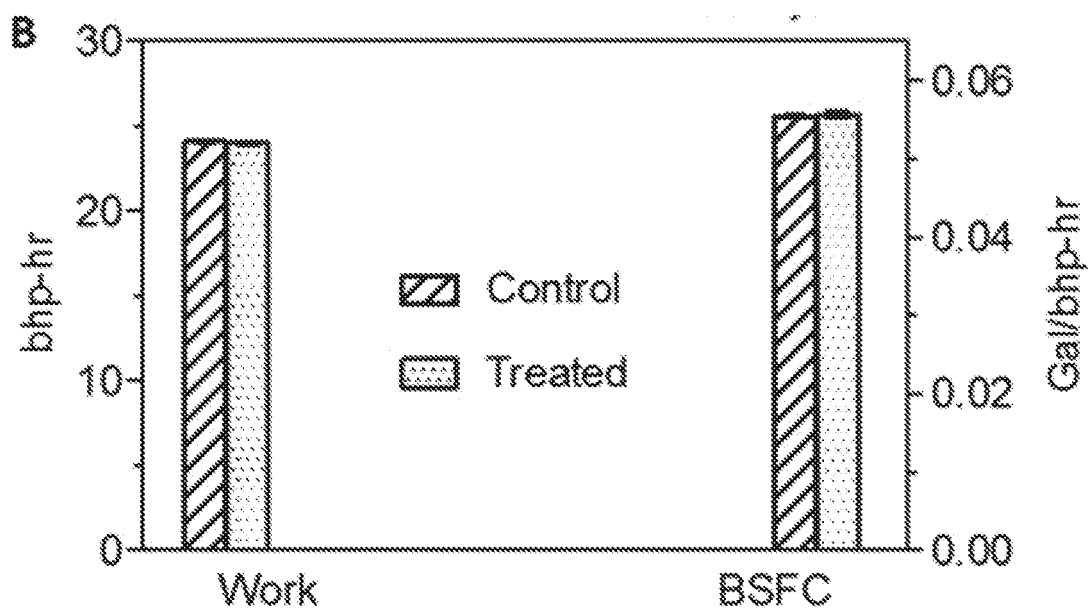
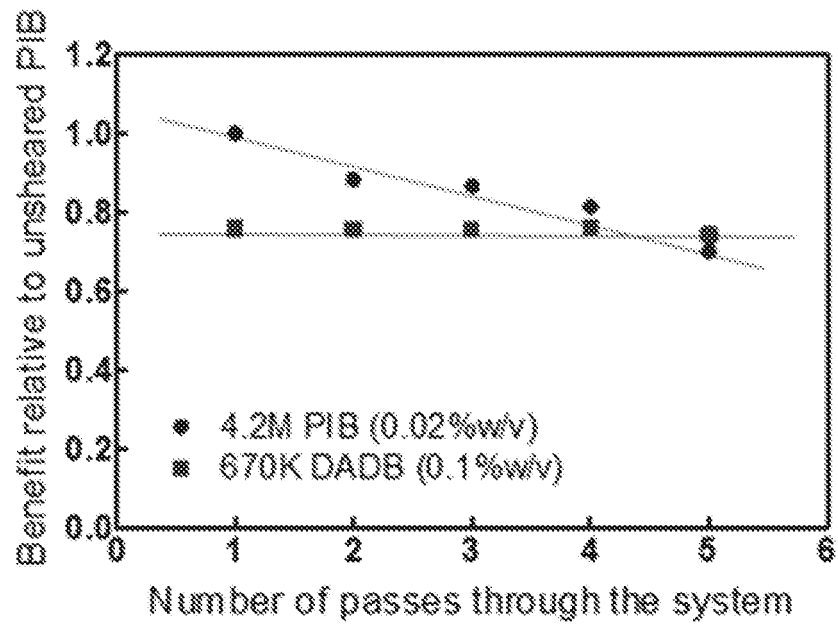
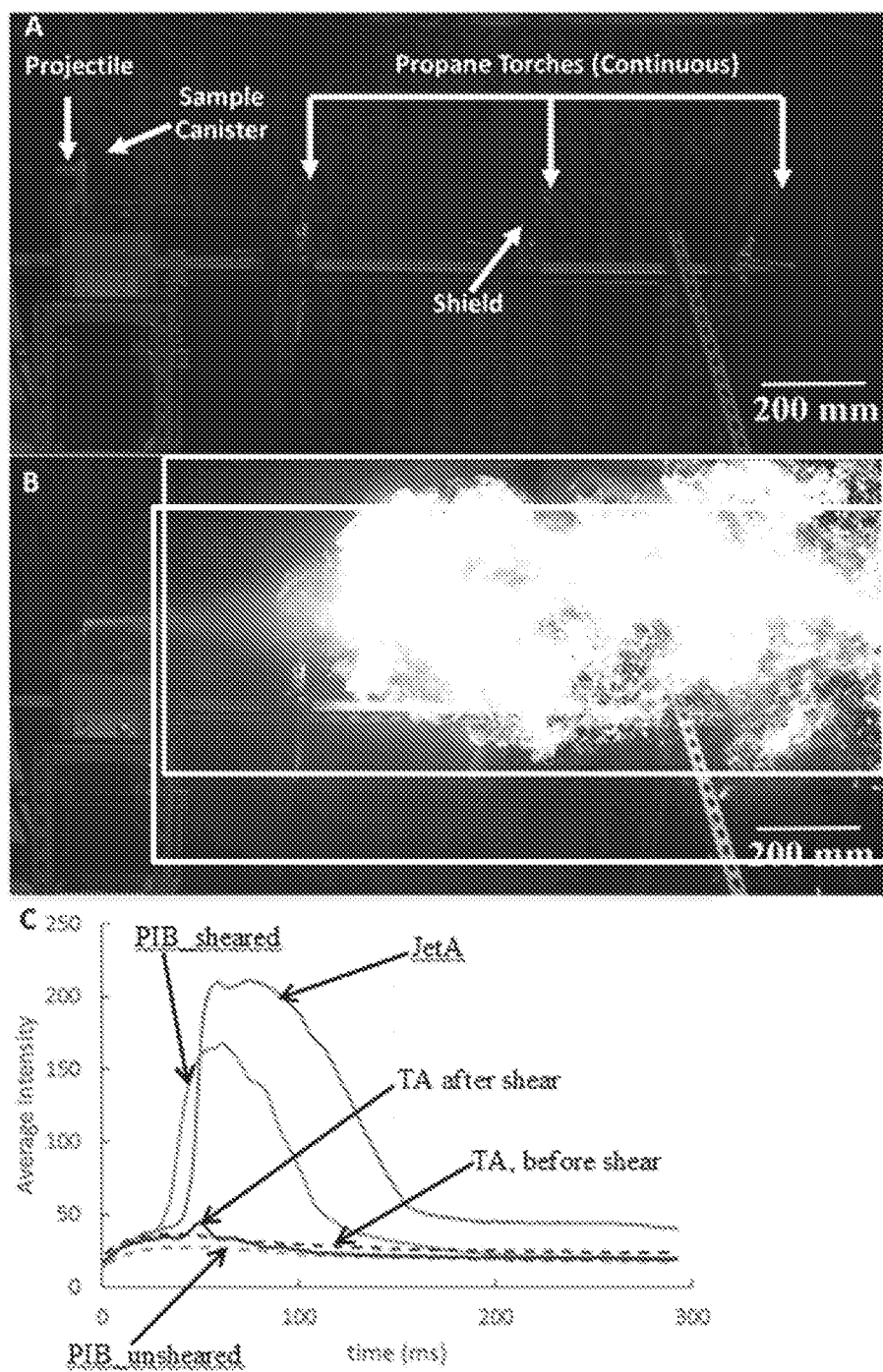


FIG. 67B

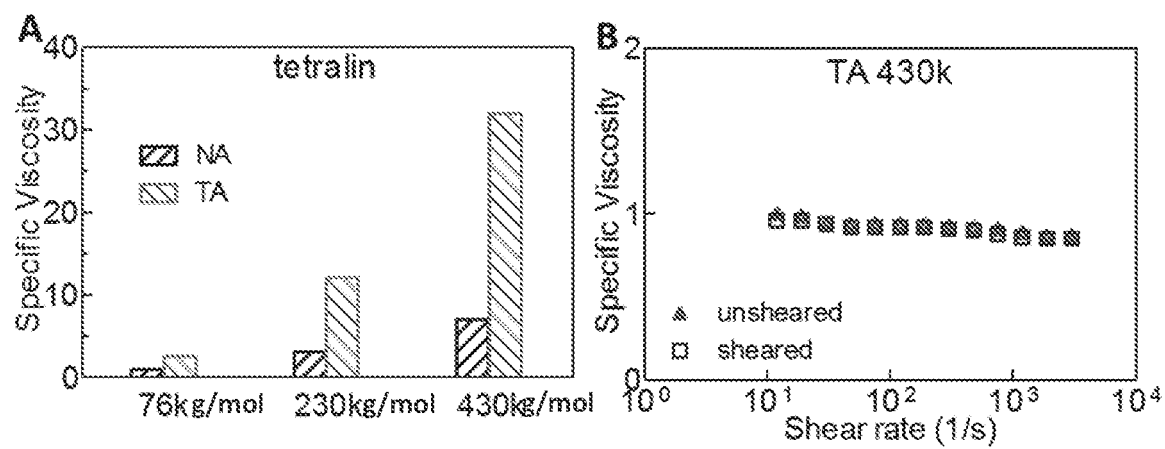
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**FIG. 68**

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**FIG. 69**

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**FIG. 70**

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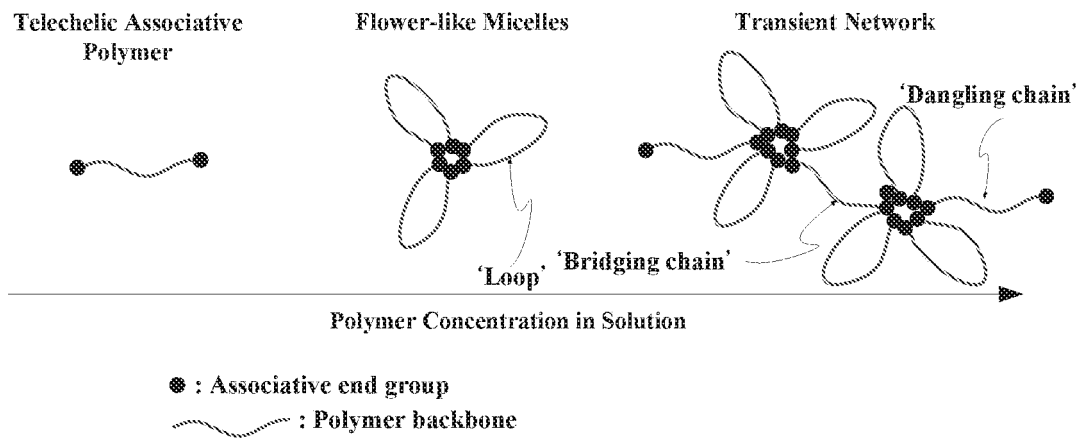


FIG. 71

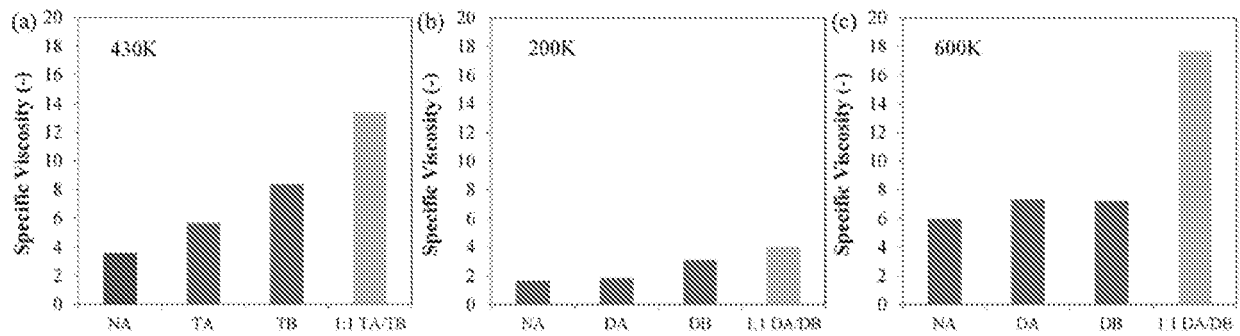


FIG. 72

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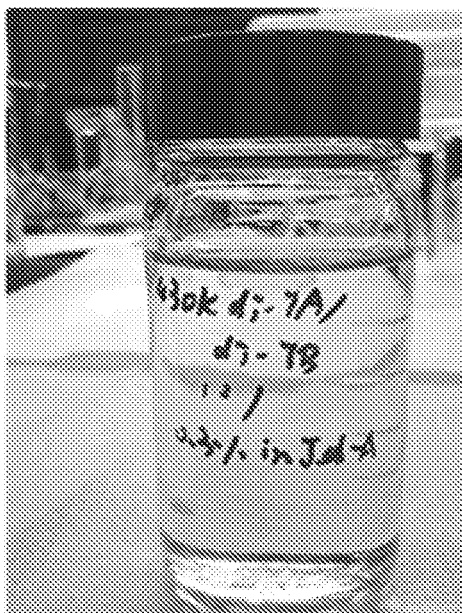
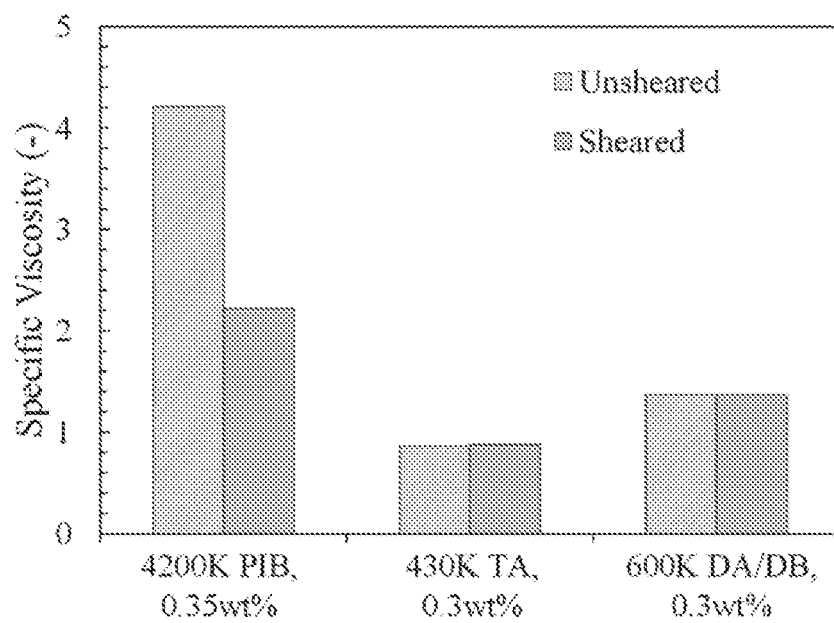
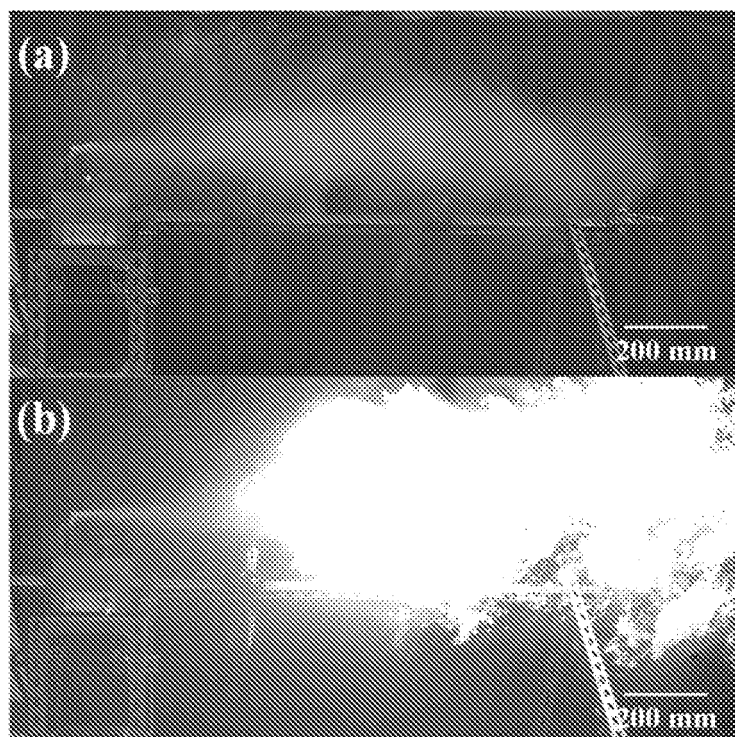
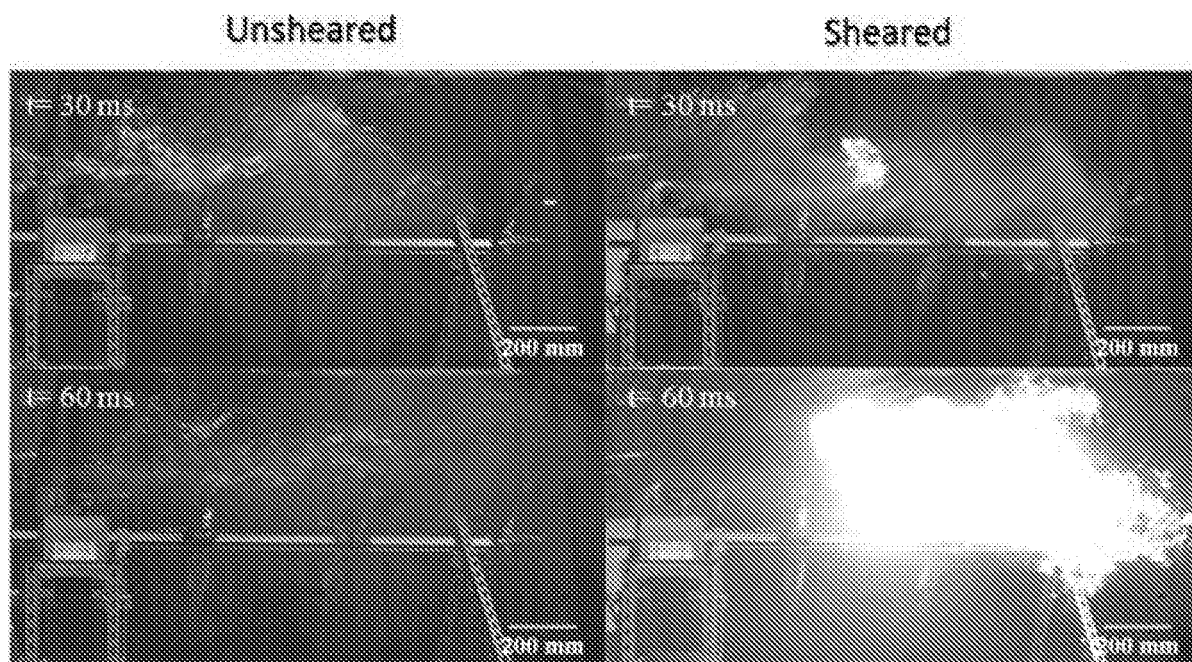
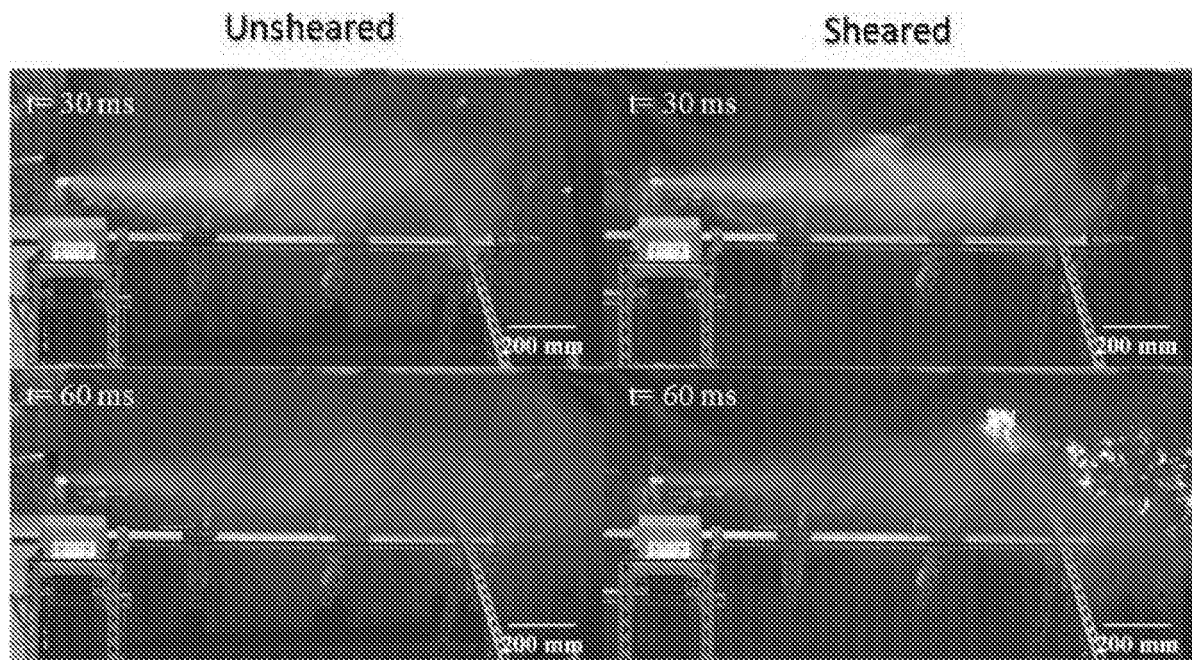


FIG. 73

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**FIG. 74****FIG. 75**

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**FIG. 76****FIG. 77**

Polymer	Solubility in Fuel	E _a of Thermal Backbone Scission (kJ/mol)
4.2M PIB	Excellent	42
FM-9	Very poor	99
Polycyclooctadiene (PCOD)	Excellent	181



FIG. 78

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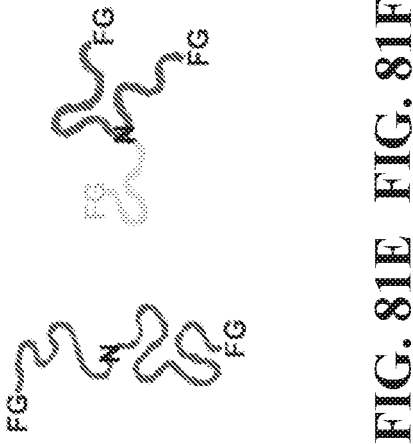
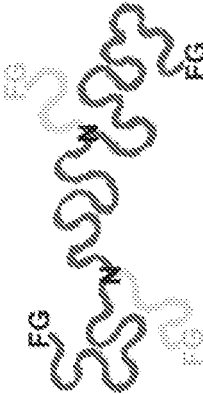
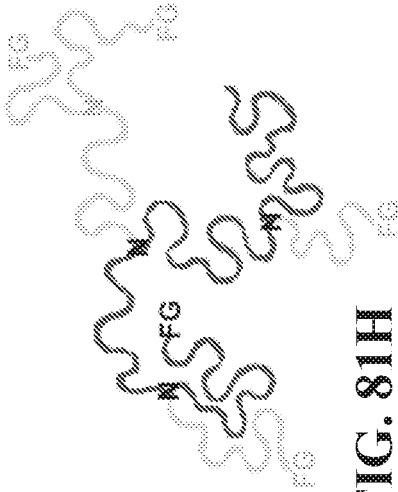
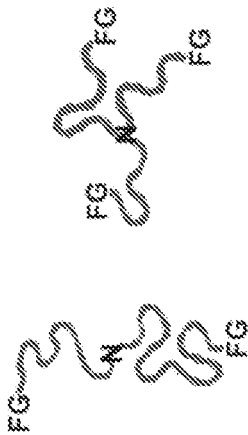
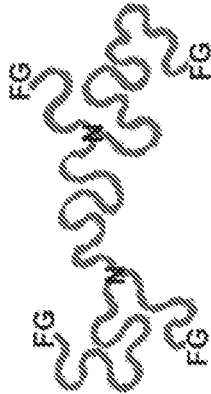
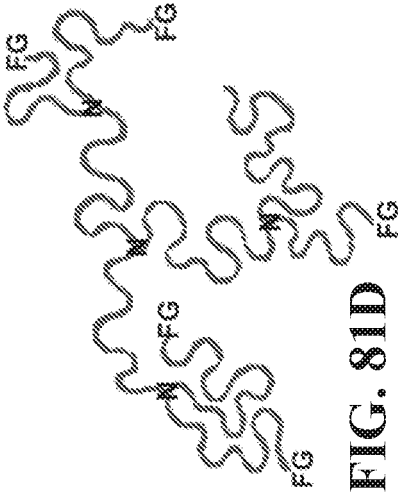
	Cyclohexane (CH)	Tetralin
Dielectric constant (ϵ) at 25°C	2.02	2.77
Refractive Index (n) at 20°C	1.426	1.541

FIG. 79

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Property	Base fuel	1000 ppm ^(a)	3000 ppm ^(a)
Flash point^(b) (ASTM D93)	65.0 °C	64.5 °C	64.5 °C
Acid No.^(c) (ASTM D3242)	0.004 mgKOH/g	0.003 mgKOH/g	0.004 mgKOH/g
Density^(d) @15°C (ASTM D4052)	0.8107 kg/L	0.8108 kg/L	0.8109 kg/L
Viscosity^(e) @-20°C (ASTM D445)	4.8 mm ² /s	6.3 mm ² /s	12.0 mm ² /s

FIG. 80



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Fluid	Viscosity
	($N\ s/m^2$, $Pa\ s$)
Acetone	0.000316
Alcohol, ethyl (ethanol)	0.001095
Castor Oil	0.650
Chloroform	0.00053
Decane	0.000859
Dodecane	0.00134
Heptane	0.000376
Hexane	0.000297
Kerosene	0.00164
Linseed Oil	0.0331
Octane	0.00051
Toluene	0.000550
Turpentine	0.001375

FIG. 82

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component	T/K	$10^{-3} \rho/\text{kg}\cdot\text{m}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
		exptl	literature	exptl	literature
cyclohexane	283.15	0.78795	0.78779 ¹⁰	1.18040	1.189 ¹⁰
	293.15	0.77870	0.77853 ¹⁰	0.98467	0.9769 ¹⁰
	303.15	0.76920	0.76918 ¹⁰	0.83400	0.8187 ¹⁰
	313.15	0.75965	0.75971 ¹⁰	0.71086	0.6980 ¹⁰
	323.15	0.74990	0.75011 ¹⁰	0.61937	0.6037 ¹⁰
toluene	283.15	0.87610	0.87611 ¹⁰	0.6659	0.6695 ¹¹
	293.15	0.86675	0.86685 ¹⁰	0.5960	0.5882 ¹¹
	303.15	0.85748	0.85754 ¹⁰	0.5368	0.5219 ¹¹
	313.15	0.84808	0.84821 ¹⁰	0.4858	0.4670 ¹¹
	323.15	0.83870	0.83871 ¹⁰	0.4400	0.4208 ¹¹
<i>cis</i> -decalin	283.15		0.9044 ¹⁴		4.092 ¹⁴
	293.15		0.8968 ¹⁵		3.355 ¹⁵
	303.15		0.8891 ¹⁵		2.704 ¹⁵
	313.15		0.8815 ¹⁵		2.214 ¹⁵
	323.15		0.8739 ¹⁵		1.861 ¹⁵
<i>trans</i> -decalin	283.15		0.8774 ¹⁴		2.578 ¹⁴
	293.15		0.8697 ¹⁵		2.107 ¹⁵
	303.15		0.8620 ¹⁵		1.760 ¹⁵
	313.15		0.8544 ¹⁵		1.499 ¹⁵
	323.15		0.8472 ¹⁵		1.283 ¹⁵

FIG. 83

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Average Bond Enthalpies (kJ/mol)**Single Bonds**

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O ₂	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

FIG. 84

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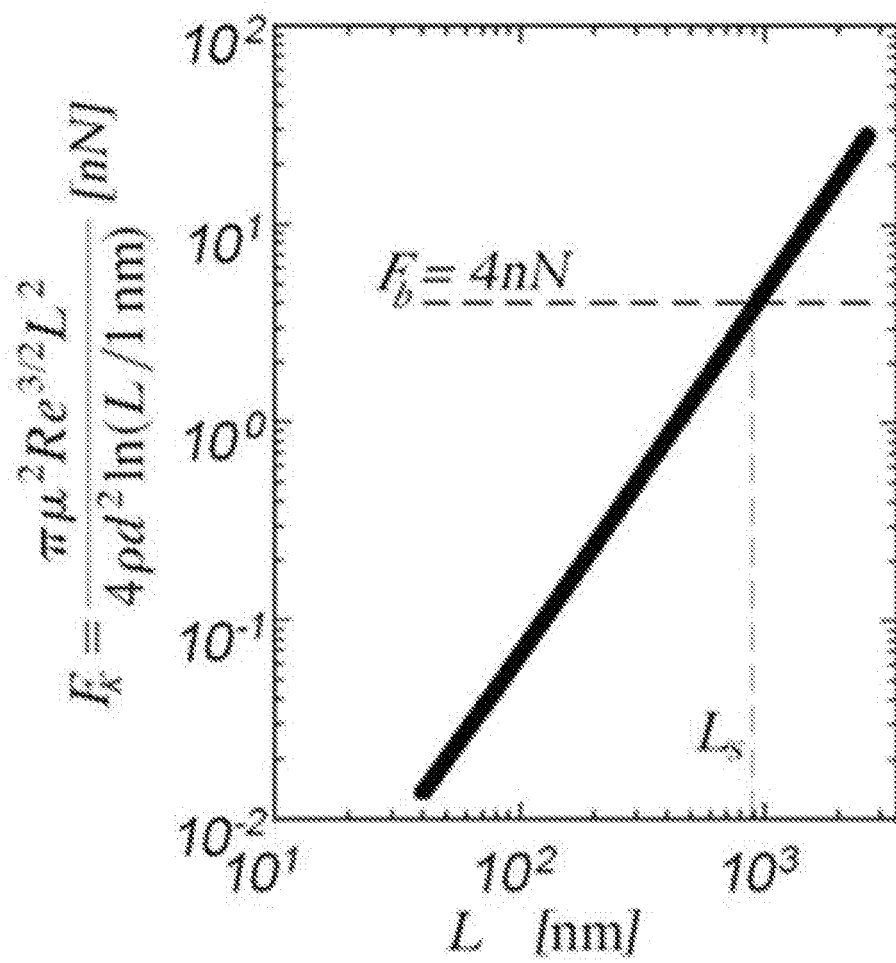


FIG. 85

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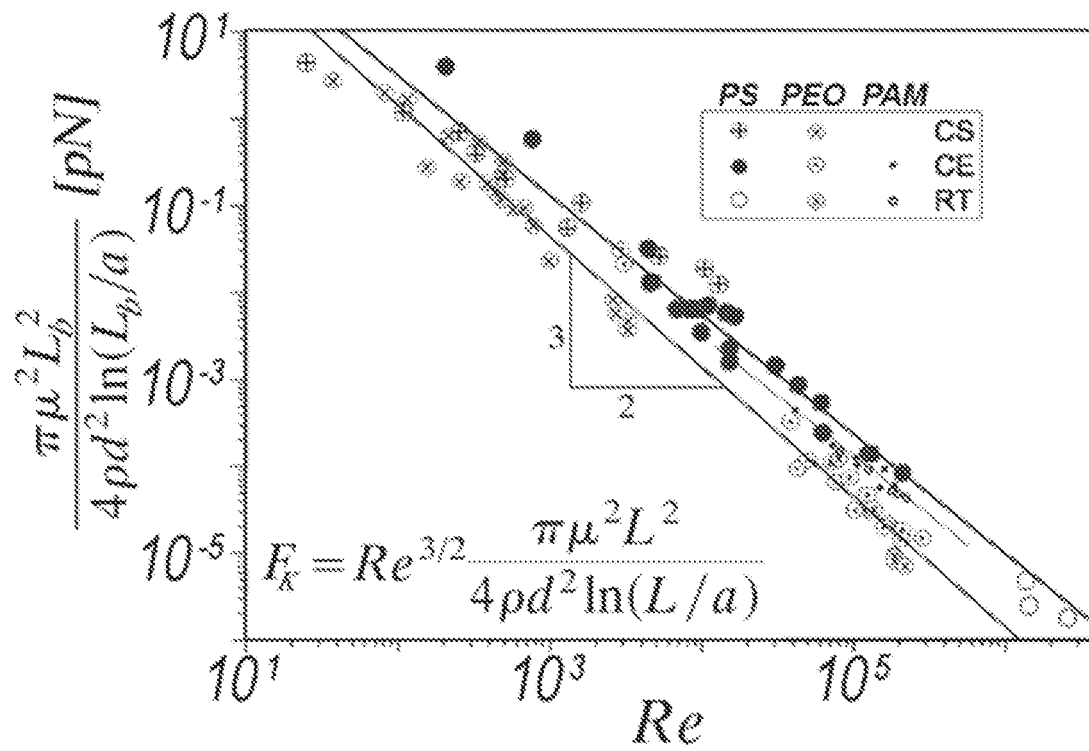


FIG. 86

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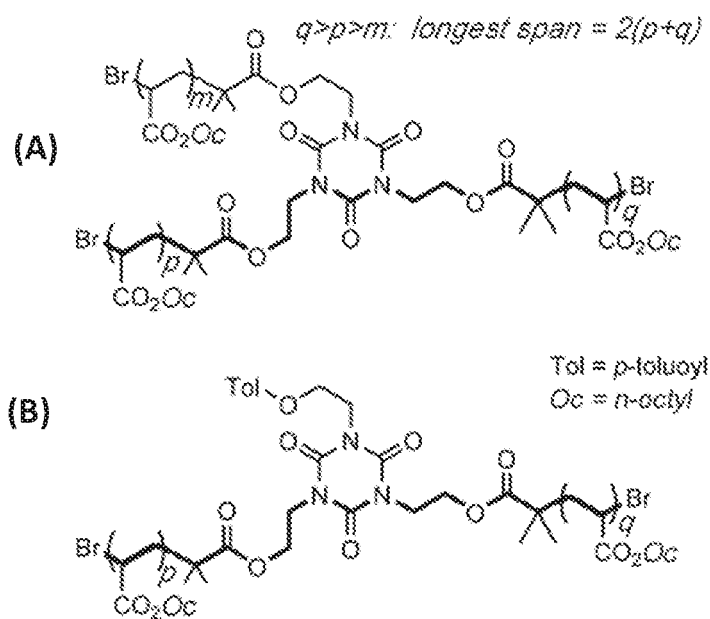


FIG. 87

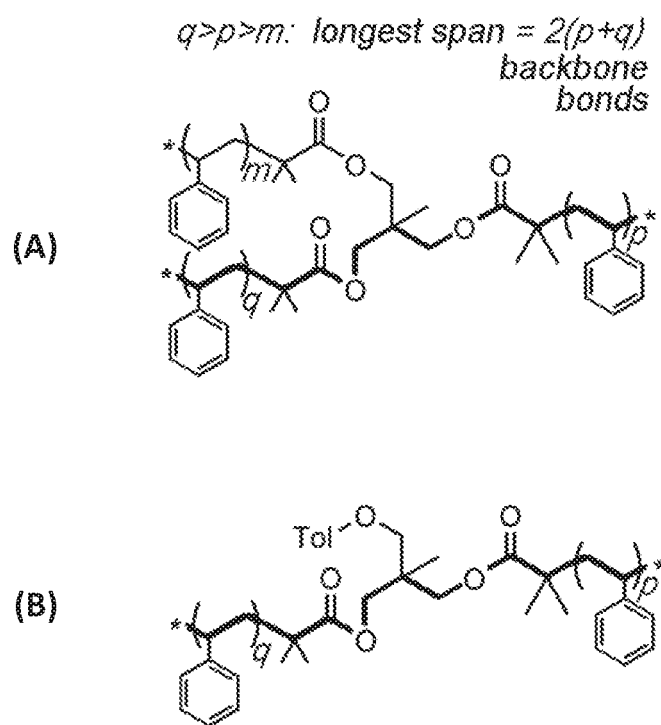


FIG. 88

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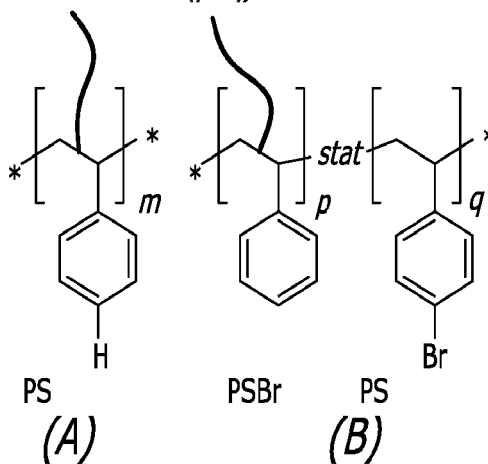
 $2m$ backbone bonds $2(p+q)$ 

FIG. 89

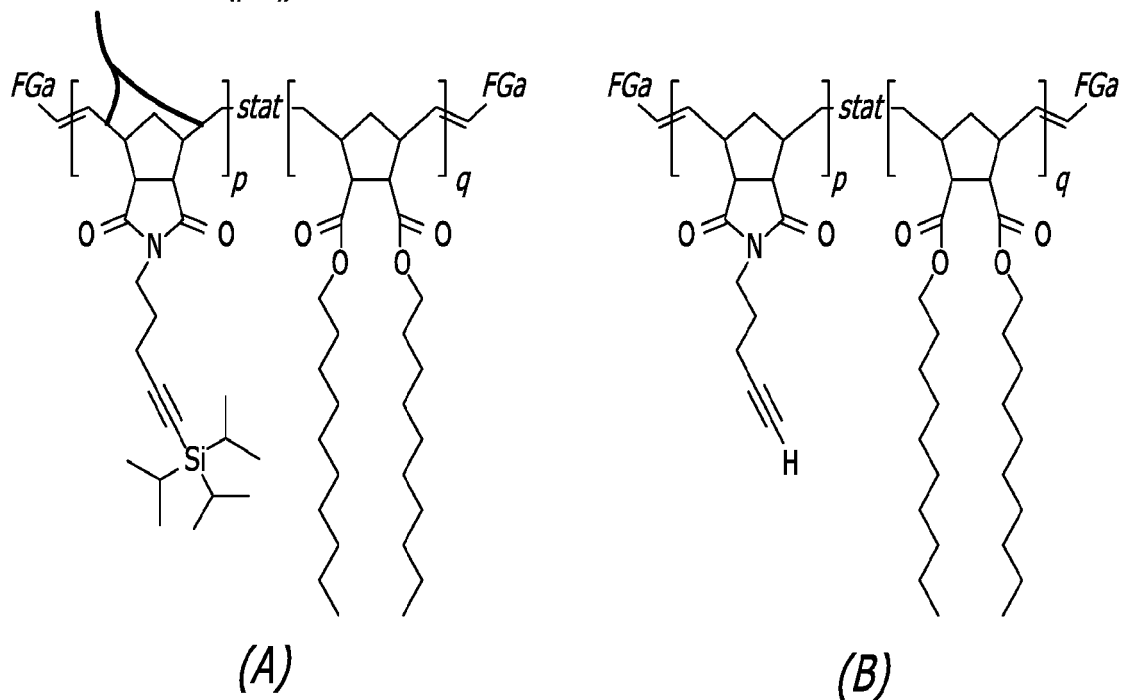
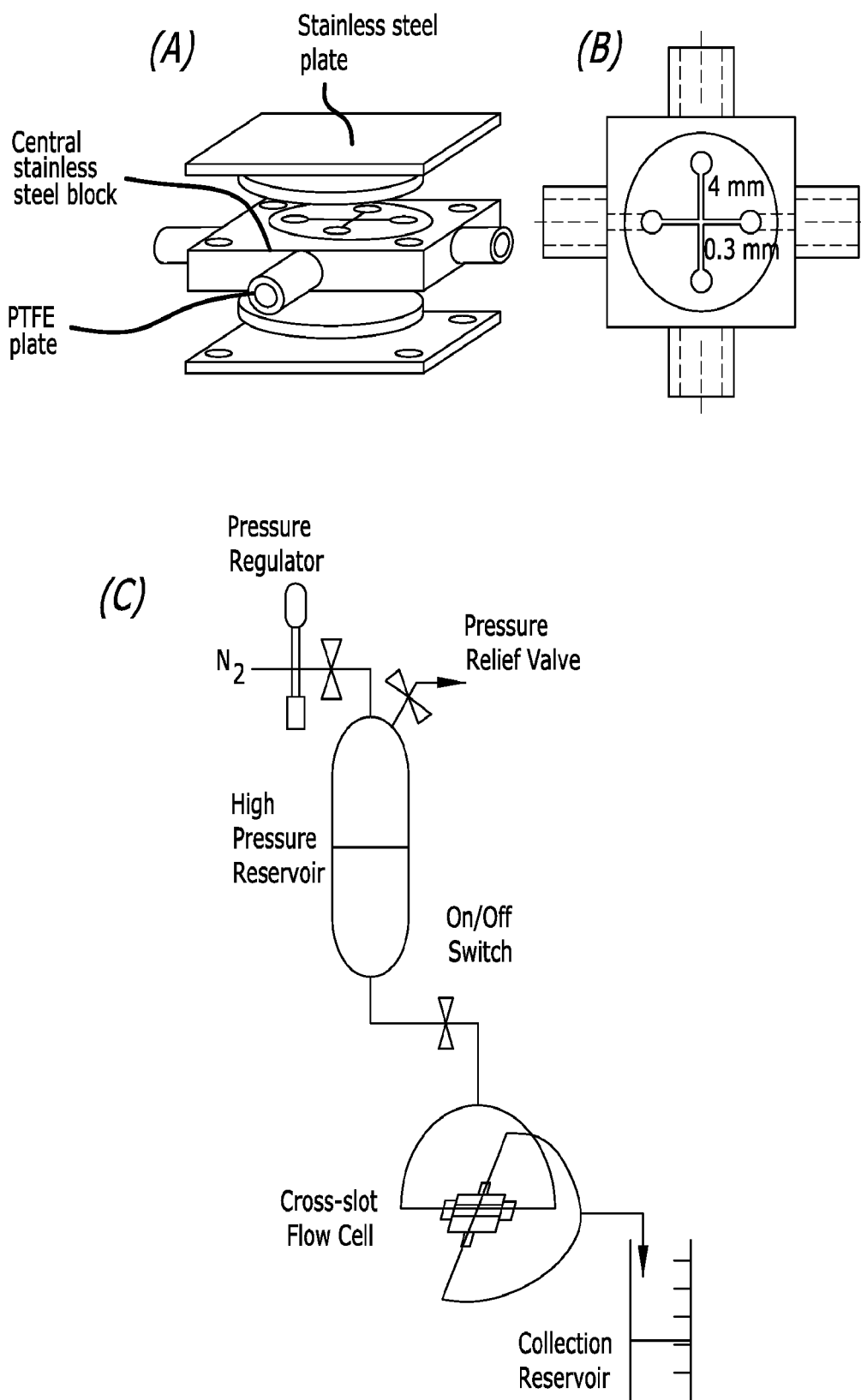
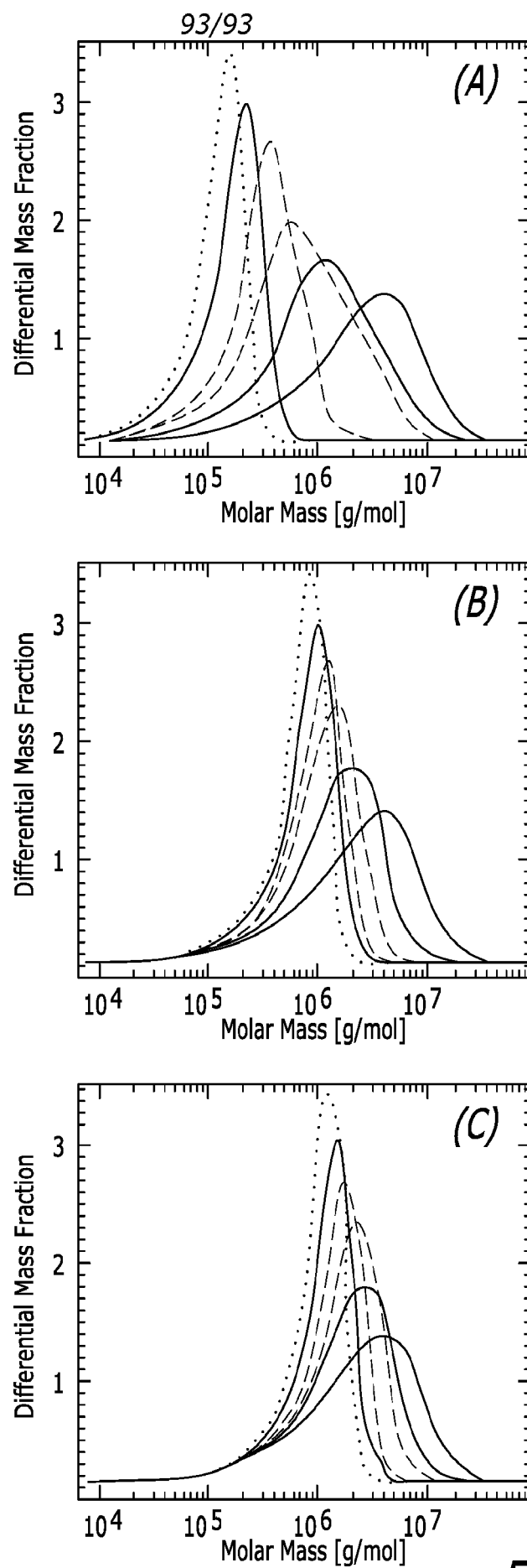
backbone bonds $5(p+q)$ 

FIG. 90

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**FIG. 91**

**FIG. 92**