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Atom transfer radical polymerization of some vinyl monomers catalyzed by imine macrocycle copper (I) complex

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Abstract

Imine macrocyclic ligand (M_1) was used in conjunction with CuBr as novel catalytic system in atom transfer radical polymerization (ATRP) of methylmethacrylate (MMA), butylmethacrylate (n-BuMA) and 2- dimethylaminoethylmethacrylate (DMAEMA). Two different initiators were involved such as Br-methoxypolyoxy-ethylene macroinitiator and 1, 3, 5-(2-bromo-2`-methylpropionato) benzene three arm star initiator. The polymerization reactions were conducted at 90°C in toluene. The macrocyclic ligand M_1 demonstrated peculiar behavior which was monitored by the GPC measurements whether with respect to the polydispersities or the molar masses. High molar masses than expected were obtained except incase of DMAEMA monomer. The structures of the formed polymers were proven via ^{1}HNMR.

Keywords

Imine macrocycles, vinyl monomers, macroinitiators, ATRP, Star- polymers

Introduction

Atom transfer radical polymerization (ATRP) is considered as the most important and widely applicable controlled free radical polymerization technique. [(1)] Most of vinyl monomers have been polymerized through ATRP such as styrenic, methacrylic, and acrylic monomers to yield well defined polymers with various architectures. [(2-4)] ATRP is believed to proceed via the establishment of fast equilibrium between dormant halogen end-capped polymer chains and active propagating radicals. [(5)] Different transition metal complexes have been utilized for this role such as the complexes of Ru, Ni, Rh, Fe and Cu. [(6-8)] However, Cu(I) halides complexed by nitrogen based ligands seem to be extremely effective in the atom transfer radical polymerization of vinyl monomers. Several ligands have been incorporated in successful Cu- based ATRP processes such as 2, 2′ bipyridine, 1, 10 phenanthrolines and N-alkyl-2-pyridinemethanimines. [(9-11)]
Also, disubstituted bipyridines were involved to form homogeneous reaction mixtures. [(9)] However, more reactive ligands were used as linear aliphatic amines, terpyridyl,

picolyl and hexahydrotriazine with three N-functionalized arms (T-triazine). [12-15] Branched aliphatic amine ligands such as tris(2-dimethylaminoethyl) amine (Me_6TREN) were found to be the most efficient ATRP catalysts that have been reported to date.[16,17] New type of ligands based on macrocyclic compounds became of growing interest because their structures provided extraordinary binding, complexation and self-assembling properties. Accordingly, ligands such as 1, 4, 8, 11-tetraaza-1, 4, 8, 11-tetramethylcyclotetradecane (Me_4CYCLAM) and 5, 5, 7, 12, 12, 14-hexamethyl-1, 4, 8, 11-tetraazamacrocyclotetradecane (Me_6 [14] aneN_4) have been reported as good ATRP ligands. [18] Recently, Imine macrocycles with more than one active center have been prepared. Those macrocycles are suitable for the complexation of two or more metal atoms and can reorient these centers relative to each other. In close relation, such compounds could give new impulses to the field of homogeneous and heterogeneous catalysis, in that they may provide enzyme-like activity and selectivity. [19] Hence, imine macrocycles M_1 which contain (2+2) active centers as in figure (1) successfully performed ATRP of methylmethacrylate, styrene and methylacrylate by using active initiating systems with respect to each monomer. [19] In case of using the macrocyclic ligand M_1, it was found, the importance of adjusting the molar ratios of the reactants to reduce the steric hindrance effect of the macrocyclic moiety to save relative fast initiation and controlled reactions. In that publication, imine macrocycle (M_1) / CuBr catalytic system was used in ATRP of MMA, n-BuMA and DMAEMA in the presence of two different initiators such as Br-methoxypolyoxyethylene and 1, 3, 5-(2-bromo-2`-methylpropionato) benzene.

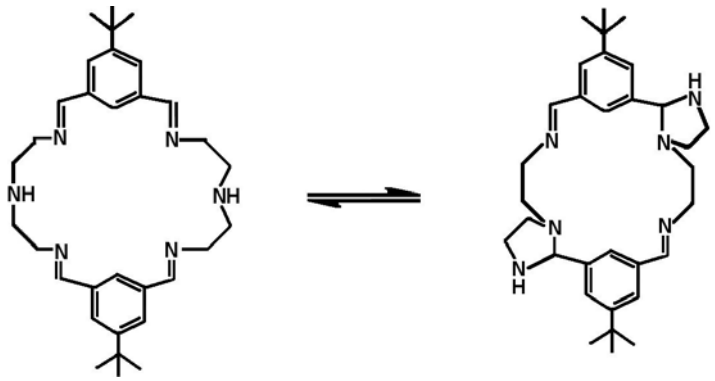


Figure 1: structure of M_1 imine macrocycle

Experimental

Materials

The monomers such as MMA, n-BuMA and DMAEMA (Aldrich) were purified via alumina column and stored under argon. The other chemicals were supplied from sigma and were used as received.

Measurements

^{1}HNMR spectra were obtained from Varian Mercury-Oxford-300 MZ by using $CDCL_3$ as the main solvent for the all samples. The molar masses and the

polydispersities were determined by using Agilent-1100 gel permeation chromatography (GPC) columns (Guard, 100, 10^4 and 10^5) fitted with G-1362 A differential refractometer using THF as the eluent with flow rate 1ml min^{-1}. Standard polystyrenes were used to calibrate the columns.

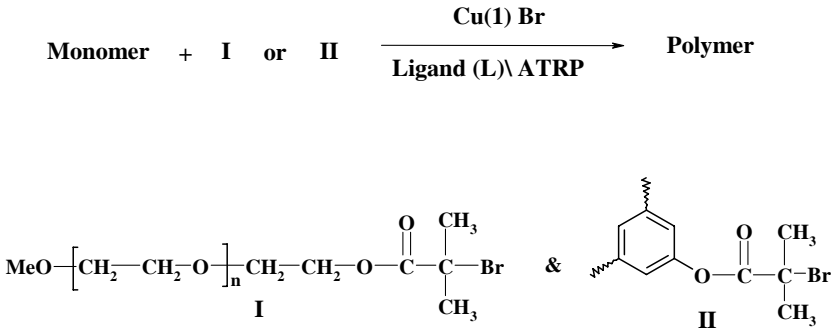
General synthetic procedures

Preparation of imine macrocyclic ligand (M_1)
A solution of 5-tert-butylbenzene-1, 3- dicarbaldehyde (3.75 mmol) in acetonitrile was added drop-wise over 2 h in an inert atmosphere to a vigorously stirred solution of diethylenetriamine (3.75mmol) in acetonitrile at room temperature. The reaction mixture was stirred for additional 24 h at room temperature. The precipitated macrocycle was filtered, washed with acetonitrile and dried under vacuum. The expected macrocycle M1 was produced as white precipitate in good yield. Analytical data to prove the structure in addition to the crystal structure can be found elsewhere in the literature. [19]

Preparation of Br-methoxypolyoxyethylene (I)
This macroinitiator was prepared from methoxypolyoxyethylene (Mn, 5000) via standard reported method by using triethylamine as the base. [20]

Preparation of 1, 3, 5-(2-bromo-2`-methylpropionato) benzene (II)
The three arm star initiator 1, 3, 5-(2-bromo-2`-methylpropionato) benzene was prepared as in the literature. [21]

Polymerization
The proper amounts of the ligand, CuBr and toluene as the solvent were added to a dry glass vial which was previously purged with argon then sealed and immersed in a thermo-stated oil bath adjusted at 90°C. The initiators were dissolved in part of toluene where the monomers and the initiators were successively added via syringes under inert atmosphere. Slow addition of the initiators was recommended for better polymerization rate in case of using those macrocycles. [19] The reactants were added in molar ratio (ligand: CuBr: initiator: monomer= 1:2:4:400) in case of Br-methoxypolyoxyethylene (I) with MMA, n-BuMA and DMAEMA monomers to form comparable polymers such as MMA-I, BuMA-I and DMAEMA-I. On the other hand, the molar ratio of the ligand: CuBr: initiator: monomer was 1:2:1:100 in case of 1, 3, 5-(2-bromo-2`-methyl- propionato) benzene (II) with the same monomers to form the three arm star polymers as MMA-II, BuMA-II and DMAEMA-II. The used amounts of the reactants were calculated as the following: In case of I: M_1 (1.03g, 2 x 10^{-3} mol), CuBr (0.57g, 4 x10^{-3}mol) and I (41.19 g, 8 x10^{-3}mol). Also, in case of II: M_1 (1.03g, 2 x 10^{-3}mol), CuBr (0.57g, 4 x 10^{-3}mol) and II (1.14g, 2 x 10^{-3}mol). The monomer ratios in case of using both of I and II were 0.8 mol and 0.2 mol, respectively according to each monomer. After definite time interval, the vial was opened and the formed polymer was dissolved in tetrahydrofuran (THF) and precipitated in n-hexane. The conversion was determined gravimetrically. The molar masses (M_{nGPC}) and the polydispersities (D) were determined via GPC by passing the polymer solution in THF through an alumina column, concentrating in vacuo and re-precipitating in n-hexane. The precipitated polymer was collected and dried under vacuum. The structures of the formed polymers were identified by ^{1}HNMR. The polymerization process can be represented as in Scheme (1).



Scheme 1: Schematic representation for the ATRP processes

Results and Discussion

In that publication, macrocyclic ligand M_1 / CuBr catalytic system was involved in the ATRP of MMA, BuMA and DMAEMA by using two different initiators such as Br-methoxypolyoxyethylene macroinitiator (I) and 1, 3, 5-(2-bromo-2`-methyl-propionato) benzene (II). According to previous studies, [19] it was elucidated that macrocyclic ligand M_1 includes two active centers. Therefore, the recommended molar ratio of M_1: CuBr: Initiator: monomer was 1:2:4:400 in favor of higher initiator percent with respect to the catalyst to overcome the steric hindrance effect of the macrocyclic moiety which may delay the polymerization reactions. Consequently, relative fast initiation and controlled reactions were saved. [19] The previous ratio was used in case of initiator (I). However, with respect to the three arm star initiator (II), the percentage for M_1: CuBr: Initiator: monomer would be 1:2:1:400 because the initiator itself contains three functional centers. Therefore, that percentage was considered as an adequate one for successful polymerization reactions. Generally, the conversion increased linearly with time. The polymerization seemed to be faster in case of DMAEMA than MMA and n-BuMA whether in case of initiator (I) or (II). Also, the polymerization reactions with respect to the three arm star initiator (II) were much faster than that with respect to the macroinitiator (I) as in tables (1, 2). The low conversions in case of MMA and n-BuMA by using I as initiator may be referred to the low initiation efficiency and hence the selectivity of I as macroinitiator toward those two monomers than that in case of DMAEMA .[19] Linear kinetic plots were observed in each case. The polydispersity recorded high values at the beginning of the reactions. The high polydispersities at the beginning may be ascribed to the slower initiation rates which increased gradually by the progression of the reaction. Also, higher molar masses than expected were observed in case of MMA and n-BuMA. That strange behavior was previously recorded and was attributed to the nature of the macrocycles themselves and their steric and electronic influences. [19] On the other hand, different behavior was recorded with respect to DMAEMA where the obtained molar masses were lower than expected and may be attributed to the adsorption of DMAEMA polymers on the GPC column as was previously reported. [22] Generally, controlled ATRP processes were obtained with characteristic variations which were committed under the influence of the macrocycle M_1. [19] The structures of the formed polymers were further proven via ^{1}HNMR as in Figures (3, 4). As shown in figure (3), with respect to MMA-I polymer, obvious signals were recorded at: δ= 0.8 - 1.3 ppm

(CH3 groups); δ= 1.3 - 2 ppm (CH_2 groups), very sharp band at δ= 3.6 ppm (OCH_3 and $COOCH_3$) and δ= 3.8-4 ppm (2 CH_2 groups beside terminal methoxy group). In case of n-BuMA, higher intensity of CH_2 groups appeared at δ= 1.3 - 2 ppm and three signals appeared in different intensities at δ= 3.6, 4 and 4.2 ppm (OCH_3, CH_2 groups of ester and those beside the terminal methoxy group). With respect to DMAEMA-I, in addition to some comparable signals as in case of MMA and n-BuMA, two different signals appeared at 2.3 and 2.6 ppm (CH_3N and CH_2N). In case of MMA-II, BuMA-II and DMAEMA-II as in figure (4), new signals appeared due to the presence of the phenyl group at δ= 7.3- 7.4 ppm. The characteristic bands of initiator I disappeared and new characteristic bands for each monomer appeared as was previously described. Generally, the macrocyclic ligand (M_1) gave comparable results in case of the three arm star macroinitiator (II) as was previously mentioned in case of the other ligands. [21] Therefore, no need appeared for further evidences on the formation of the star polymers.

Conclusion

Imine macrocycle (M_1) was successfully used to some extent as good catalytic system in the ATRP of MMA, n-BuMA and DMAEMA with Br-methoxypolyoxyethylene macroinitiator and 1, 3, 5-(2-bromo-2`-methyl- propionato) benzene three arm star initiator. The three arm star initiator performed faster polymerization than in case of the macroinitiator because of its higher reactivity which could save faster initiation and controlled reaction. Obvious higher molecular weights and polydispersities than expected were obtained due to the steric and electronic effects of those macrocycles that slowed down the polymerization reactions and caused that behavior. DMAEMA polymers showed different behavior due to the special nature of the monomer itself as was previously described.

Table 1: ATRP of MMA, n- BuMA and DMAEMA initiated with Br-methoxypolyoxyethylene

Entry	Time (h)	Conversion (%)	M_{nth}	$M_{n\,GPC}$ g/ mol	D
A_1	1	19	7051	8950	1.7
A_2	2	25	7652	9560	1.49
A_3	3	30	8153	10110	1.32
A_4	4	32	8353	10250	1.2
A_5	6	34	8553	10560	1.17
A_6	24	35	8653	10700	1.3
B_7	2	20	7993	9860	2
B_8	3	22	8277	10350	1.19
B_9	4	25	8704	10960	1.16
B_{10}	5	28	9131	12280	1.15
B_{11}	6	30	9415	13154	1.24
B_{12}	24	32	9699	14030	1.32
M_{13}	2	51	13167	11270	1.4
M_{14}	3	63	15054	13154	1.32
M_{15}	4	72	16469	14470	1.3
M_{16}	5	80	17727	15700	1.15
M_{17}	6	86	18670	16720	1.2

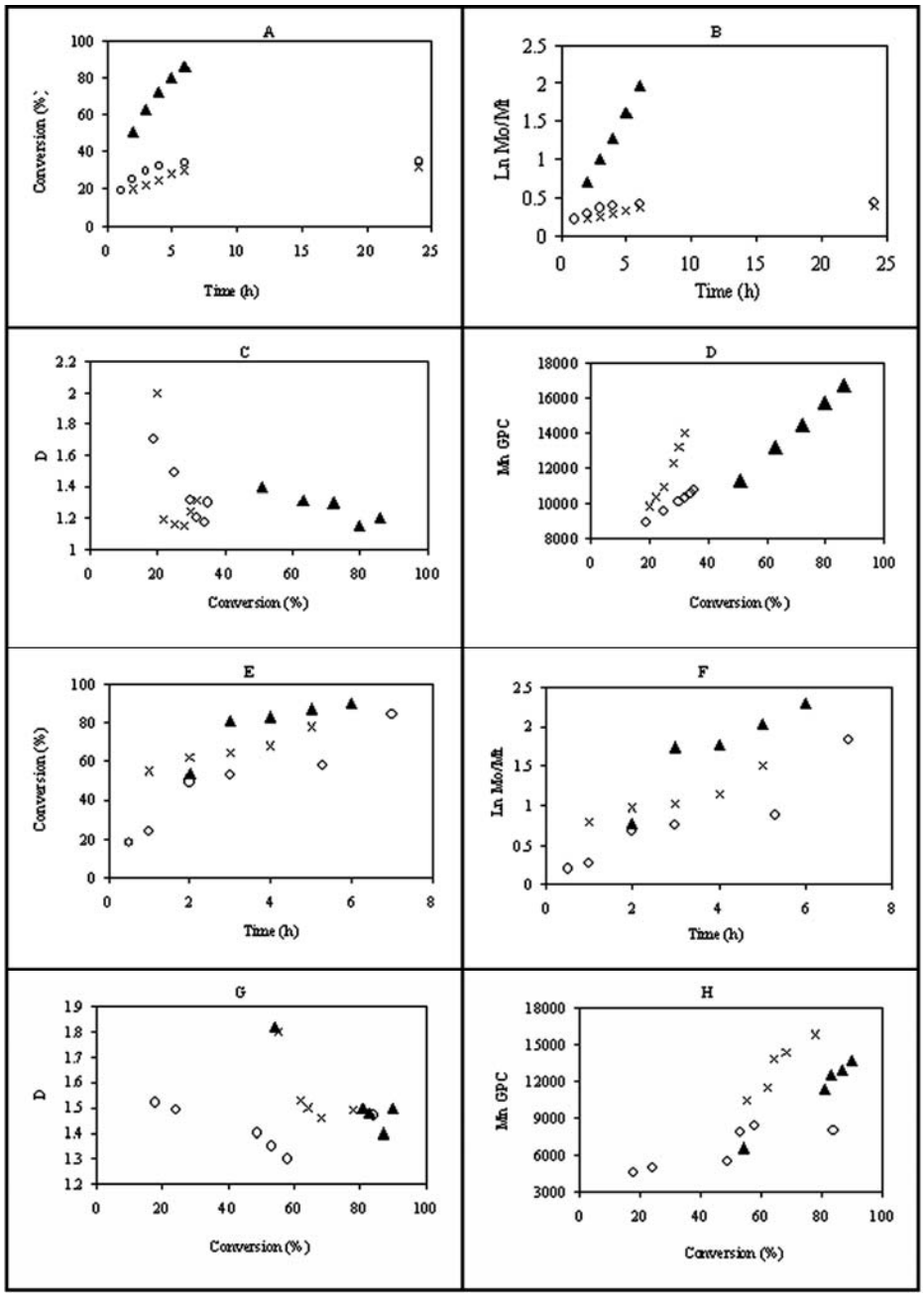


Figure 2: kinetic plots for ATRP of MMA, n- BuMA and DMAEMA initiated with initiators I (A-D) and II (E-H)

Table 2: ATRP of MMA, n- BuMA and DMAEMA initiated with 1, 3, 5-(2-bromo-2`-methyl-propionato) benzene

Entry	Time (h)	Conversion (%)	M_{nth}	$M_{n\ GPC}$ g/ mol	D
A_1	0.5	18	2374	4640	1.52
A_2	1	24	2974	4965	1.49
A_3	2	49	5477	5540	1.4
A_4	3	53	5878	7870	1.35
A_5	5.30	58	6379	8370	1.3
A_6	7	84	8982	7990	1.47
B_7	1	55	8393	10500	1.8
B_8	2	62	9388	11496	1.53
B_9	3	64	9672	13810	1.5
B_{10}	4	68	10241	14380	1.46
B_{11}	5	78	11663	15800	1.49
M_{12}	2	54	9061	6610	1.82
M_{13}	3	81	13306	11350	1.5
M_{14}	4	83	13621	12500	1.48
M_{15}	5	87	14250	12960	1.4
M_{16}	6	90	14721	13690	1.5

A, B, M refer to MMA, n- BuMA and DMAEMA, respectively

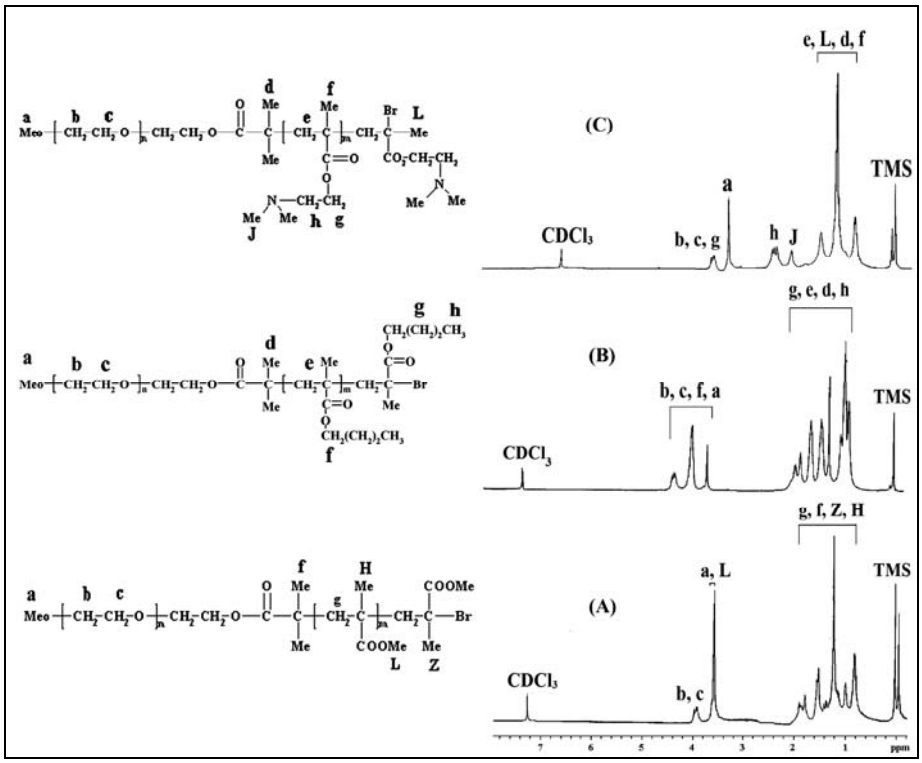


Figure 3 (A, B): [1]HNMR spectra of MMA (A) and n-BuMA (B), DMAEMA (C) polymers, respectively initiated with Br-methoxypolyoxyethylene (I)

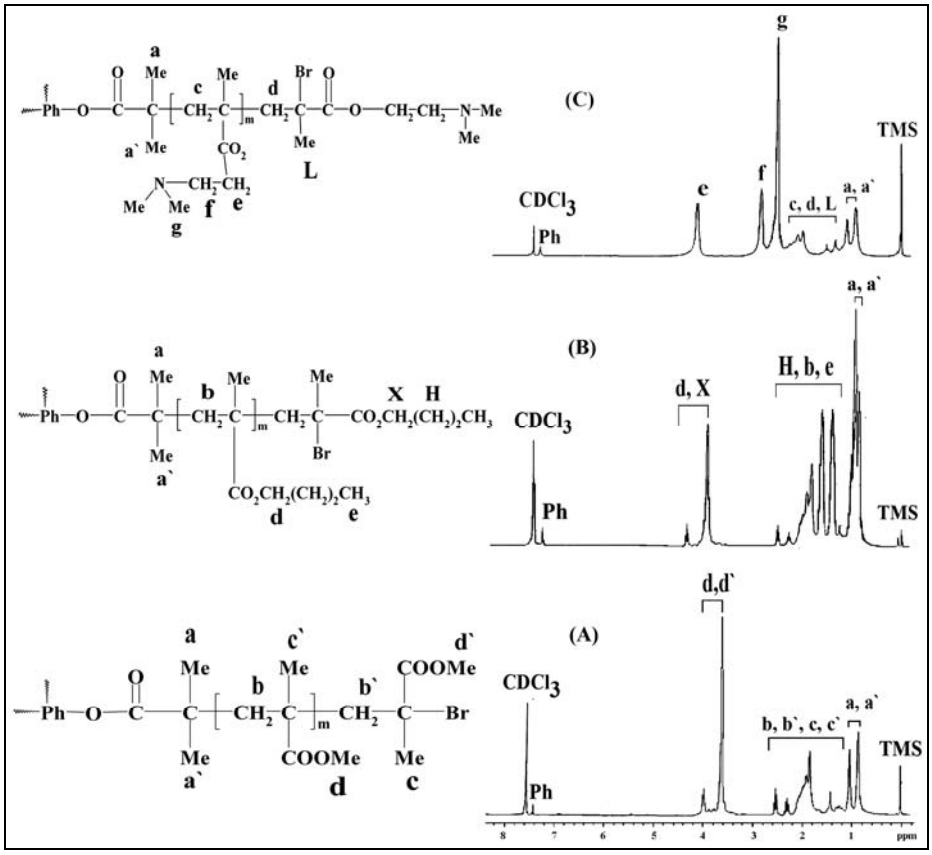


Figure 4 (A, B): [1]HNMR spectra of MMA (A), n-BuMA (B), DMAEMA polymer (C)polymers, respectively initiated with 1, 3, 5-(2-bromo-2`-methyl- propionato) benzene (II)

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