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Functionalized polyglycidol-CuCl-complexes as catalysts in the oxidative coupling reaction of terminal acetylenes

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Summary

Novel hyperbranched amino-terminated polyglycidoles have been synthesized and tested as macromolecular ligands in the oxidative coupling reaction of phenylacetylene. Amino-terminated polyglycidoles-CuCl complexes showed to be more effective catalysts than the reference monomeric tertiary amines-CuCl ones, but less effective than the most efficient N,N,N'N'-tetramethylethylenediamine-(TMDA) CuCl complex. The difference in performance of monomeric and hyperbranched ligands is probably due to two factors. The first one is better complexation abilities and the second is the local increase of reagent concentration.

Introduction

Recently, hyperbranched polymers have become of increasing interest as a potential alternative to the perfectly branched dendrimers that have to be constructed in a usually tedious, stepwise approach. Hyperbranched polymers possess all the important features of perfectly branched dendrimer and can easily be prepared by polycondensation reaction of AB_m monomers [1]. The main drawback of hyperbranched polymers obtained by hyperbranched polymerization of AB_m monomers is a broad molecular weight distribution combined with incomplete branching. Catalysis is a research area in which promising applications for hyperbranched polymers may be developed. They have nanoscopic dimensions. This combination of features makes dendrimers and hyperbranched polymers suited to close the gap between homo- and heterogeneous catalysis. There are numerous examples of successful applications of perfect dendrimers with peripheral catalysts sites as macromolecular ligands [2-10], however, to our knowledge very few efforts have been made to use hyperbranched polymers for this purpose.

The oxidative coupling of terminal acetylenes is one of the important C-C bonds forming reaction in organic chemistry allowing to synthesize polydiacetylene-containing polymers when using terminal bisacetylenes as starting monomers (11-15). In case of use O_2 as an oxidant the reaction is catalyzed by Cu^+ complexes with tertiary amines. The present authors have developed a novel technique allowing to obtain high molecular weight ($M_n=10^5$) diacetylene-containing polyesters and

polyamide by high temperature oxidative coupling of terminal bisacetylenes in N-methylpyrrolidone (NMP) or o-dichlorobenzene (o-DCB) using N,N,N',N'-tetramethylenediamine (TMDA)-CuCl complex [16,17]. The aim of this work is to investigate the possibility to use a hyperbranched ligand in oxidative coupling of terminal acetylenes. As a candidate for hyperbranched ligand precursor, polyglycidol has been chosen. This hyperbranched polymer is easy to obtain by anionic polymerization of glycidol [18]. Polyglycidol shows branching degree about 0.6 and has terminal hydroxyl groups which can easily be modified.

Experimental.

Materials

All reagents were purchased from Aldrich and used as received.

Instruments

FTIR spectra were taken using a Nikolet 510p spectrometer. NMR ^{1}H and ^{13}C spectra were obtained with a Varian spectrometer at 300 and 75.5 MHz, respectively in MeOH-(d4), DMSO-(d6) or CDCl3 with TMS as an internal standard. Gel permitting chromatography was performed on a Varian 9012 instrument at 30 C with chloroform as eluent. Calibration was conducted with polystyrene standards.

Polyglycidol (PG)

To a suspension of MeOK (0.5 g, 7 mmol) in dioxane (35 ml) glycidol (50 g, 675 mmol) was added dropwise during 12 hr at 90 C under nitrogen flow. Dioxane was distilled off under vacuum and obtained polyglycidol as a very viscous syrup was neutralized until pH=7 by conc. HCl. Yield 98 %.

Tosyl-terminated polyglycidol (Ts-PG)

To a solution of PG (17.7g) in pyridine (50ml) TsCl (50.3 g) was added dropwise at 0 C and the reaction mixture was stirred for 24 hr at room temperature. Formed pyrininium salt was filtered off, and clear viscous solution was poured into diluted HCl. The polymeric material was collected, dissolved in chloroform and washed with water. The solution was dried over MgSO4 to give very viscous clear syrup after removal of chloroform under vacuum. Yield 85%.

NR_2- terminated polyglycidols ($N(Et)_2$-PG, $N(C_5H_{11})_2$-PG)

A solution containing Ts-PG (4 g), diethylamine or di-n-penthylamine (20 ml) and dioxane (20ml) was refluxed under nitrogen for 24 hrs. The solvent and excess of amine were removed under reduced pressure. The residue was dissolved in toluene and washed by water. After drying over MgSO4 and removing toluene amine-terminated PGs were obtained as sticky solids.

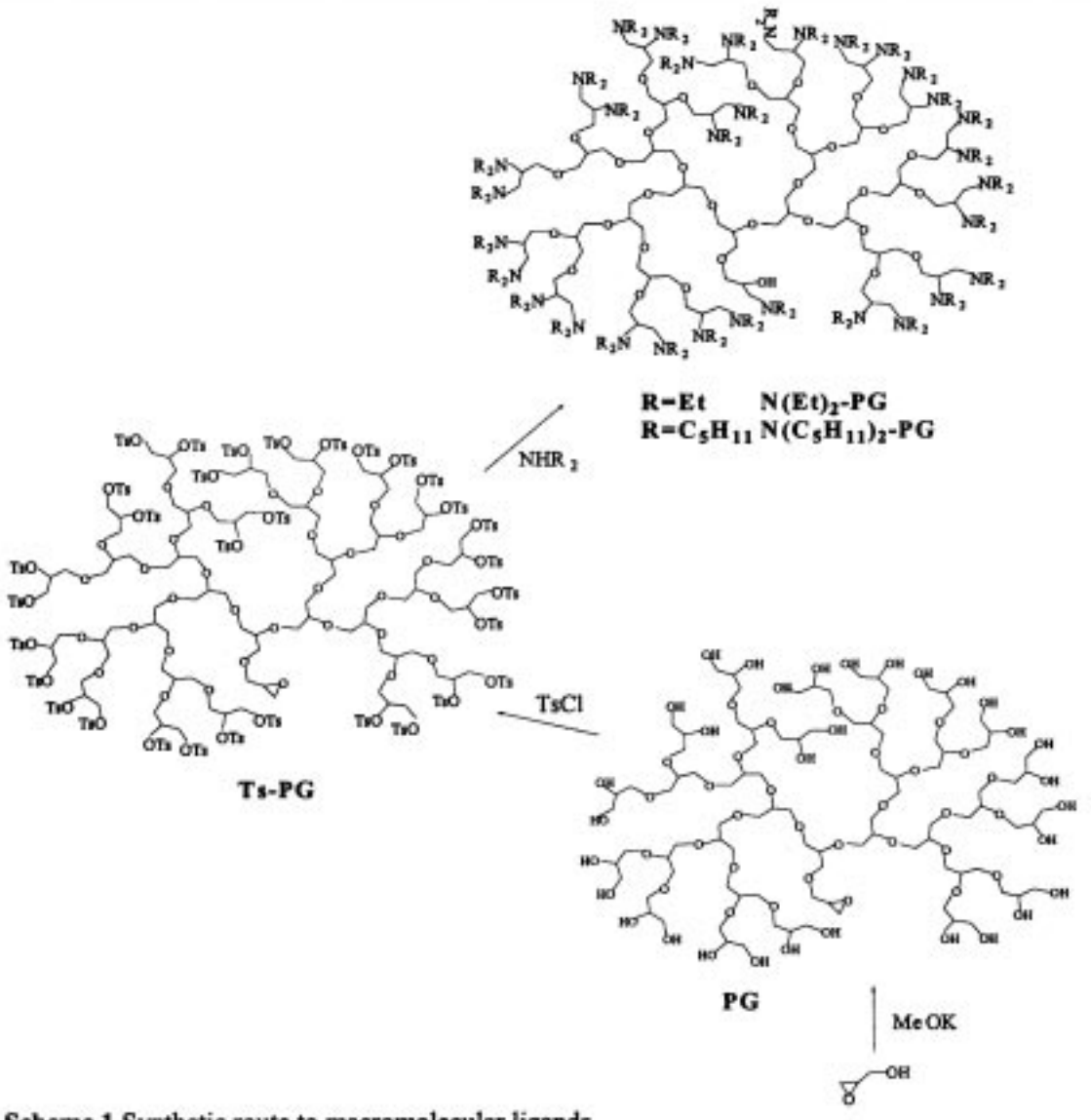
Oxidative coupling reaction

A solution containing phenylacetylene (1.1g) CuCl (0.033g) amine (0.1g) and 2-propanol (40ml) was stirred (100 rpm) 24 hrs at 21 C and oxygen flow of 20 ml/min. The solvent was eliminated in vacuum and the residue was crystallized from 2-propanol.

Molecular modeling

All calculations were carried out using Jaguar 3.5 package [19] using gradient corrected BP functional (Becke88 exchange [20] in combination with Perdew86 correlation functional [21]). LACVP(d) and LACVP(d,p) basis sets were used for geometry optimization and single point energy calculations, respectively.

Results and Discussion



Scheme 1 Synthetic route to macromolecular ligands

The main focus of this work is to study the possibility of use of macromolecular hyperbranched ligands in the reaction of oxidative coupling of terminal diacetylenes. The synthetic route to macromolecular ligands is shown in Scheme 1. The ring-opening polymerization of glycidol affords hyperbranched polymer (PG) with terminal hydroxyl groups. Terminal hydroxyls have been converted into tosilates by treating PG with TsCl in pyridine to produce Ts-terminated hyperbranched polymer Ts-PG. The last step is the nucleophylic substitution reaction of Ts-PG with secondary aliphatic amines (diethylamine or di-n-pentylamine) giving NR_2 terminated hyperbranched molecules $N(Et)_2$-PG and $N(C_5H_{11})_2$-PG, respectively. These hyperbranched polyamines were used as ligands in CuCl –catalyzed oxidative coupling reaction of phenylacetylene. Fig 1 shows ^{1}H-NMR spectra hyperbranched molecules.

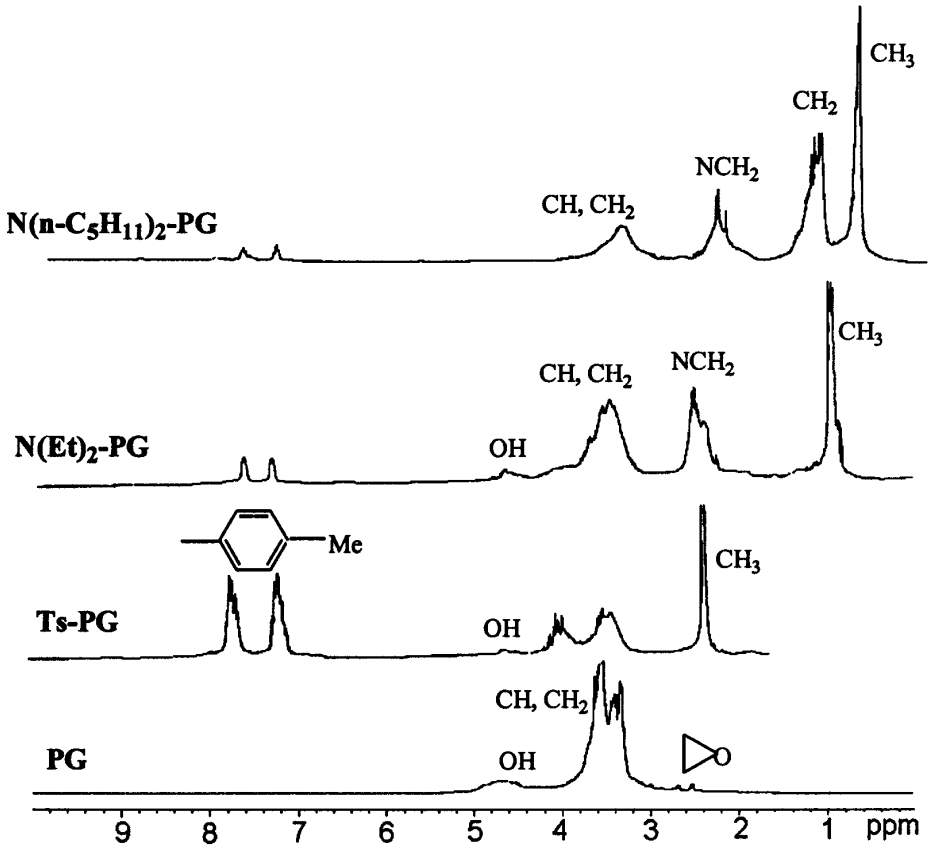


Figure 1, ^{1}H-NMR spectra of hyperbranched intermediates in DMSO-(d_6) (PG, $N(Et)_2$-PG, $N(n\text{-}C_5H_{11})_2$-PG) and in $CDCl_3$ (Ts-PG)

^{1}HNMR spectra shown in Fig 1 confirms the chemical transformation described in Scheme 1. PG shows signals corresponding to terminal OH (4.8-4.4 ppm) and aliphatic hydrogens in the range of 3.2-3.8 ppm. Small peaks at 2.4-2.6 ppm are due to oxirane ring at focal point of each macromolecule. When modified with TsCl terminal OH almost disappeared an three groups of signals corresponding to Ts group are detected in the range of 7.8-7.4 ppm (aromatic) and 2.3 (Me). The reaction with secondary amines leads to appearance of various multipletes in the region of 0.8-2.6 ppm due to aliphatic protons of alkylamino groups. Similarly to many polymeric reactions the modification of terminal groups in PG is not complete showing

conversion around 75-80 % for all modification reactions as calculated from Ts/OH and NR_2/Ts proton ratios. The chemical modification of PG strongly affects the property of hyperbranched polymer. While PG is readily soluble in methanol and water TS-PG is only soluble in nonpolar solvents like chloroform. The substitution reaction of TS-PG with secondary amines produce amine terminated PG readily soluble in alcohols but not in water. The degree of branching (DB) of PG has been estimated as described in [22] using the relative integrals from IG ^{13}C-NMR spectra according to formula:

$$DB=2D/(2D+L) \quad (1)$$

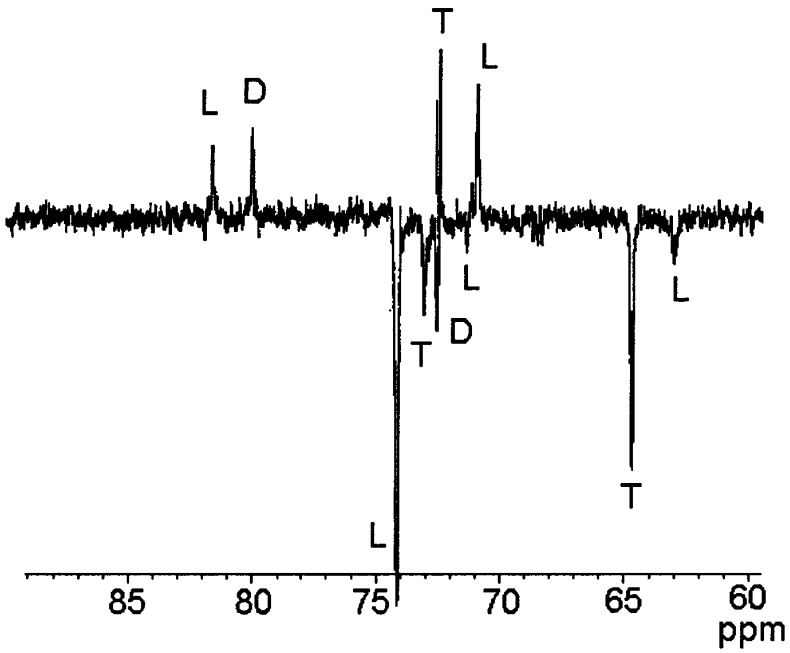
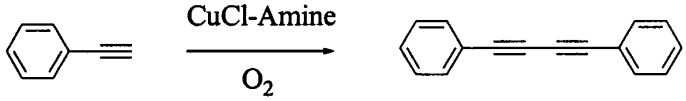


Figure 2. DEPT ^{13}C-NMR spectra of PG in DMSO-d_6. Carbons belonging to terminal, dendritic and linear units indicated as T, D and L

DB of PG was found to be of 0.51, close to random polymerization value. Fig 2 shows DEPT ^{13}C-NMR spectra and signal assignment of PG obtained by anionic polymerization of glycidol. Due to insolubility of PG in chloroform the molecular weight measurements using GPC were carried out for TS-PG. GPC data showed Mw of 7300 and polydispersity of 1.47, which is roughly corresponds to degree of polymerization (DP) of 30. Table 1 shows the results of oxidative coupling reaction of phenylacetylene (Scheme 2) using conventional TMDA-CuCl, amine-terminated PG-CuCl complexes as well as triethylamine-CuCl and tri(n-penthylamine)-CuCl complexes as references.



Scheme 2 The oxidative coupling reaction of phenylacetylene.

As a reference, monomeric tertiary amines, modeled amino groups of hyperbranched

ligands were tested as well as CuCl alone. The results show that hyperbranched ligands always favor the oxidative coupling reaction compared to monomeric triethylamine and tripentylamine. However, TMDA-CuCl is superior

Table 1 . The results of oxidative coupling reaction of phenylacetylene using different amine-CuCl complexes

Run	CuCl (g)	Amine	Reaction time (hrs)	Yield
1	0.033	-	24	<1
2	0.033	TMDA	24	96.2
3	0.033	NEt_3	24	2
4	0.033	$N(n\text{-}C_5H_{11})_3$	24	<1
5	0.033	$N(Et)_2$-PG,	24	25
6	0.033	$N(C_5H_{11})_2$-PG	24	8

The oxidation coupling reaction mechanism involves the Cu(I) amine-acetylene complex formation [23]. The tighter complex the higher acetylenic proton acidity that is known to be of importance. On the other hand the higher acidity of acetylenic proton the faster the reaction [24]. It seems that the structure of hyperbranched amine favors complex formation of amine-Cu intermediate with terminal acetylene.

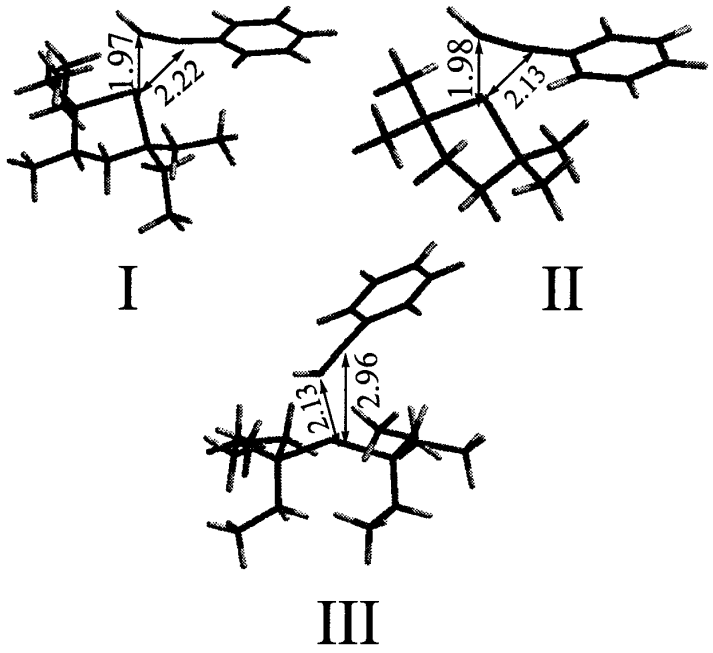


Figure 3. BP/LACVP(d) optimized geometries of Cu(I) 1,2-bis-(diethylamino)-2-methylethane phenylacetylene (**I**), Cu (I) N,N,N'N'-tetramethylethylenediamine Phenylacetylene (**II**) and Cu (I) $(triethylamine)_2$ phenylacetylene (**III**).

The theoretical analysis of this problem shows that complex **I** (Fig.3), representing a model for complexation between terminal NR_3 groups of $N(Et)_2$-PG, Cu (I) and phenylacetylene is similar to that formed by TMDA complex (**II**). On the other hand, complex **III**, formed by triethylamine is much looser. The binding energies of

phenylacetylene at BP/LACVP(d,p)//BP/LACVP(d) level for complexes **I**, **II** and **III** are -31.3, -38.9 and 36.0 kcal/mol, respectively, revealing that the formation of complex **III** is endothermic process. The binding energies of complexes correlate very well with yield of diphenyldiacetylene thus explaining better performance of hyperbranched ligand compared to low molecular weight one. Another contribution to the performance of hyperbranched ligand may come from the increase of local concentration of phenylacetylene through adsorption on surface of hyperbranched ligand. Poorer performance of , $N(C_5H_{11})_2$-PG hyperbranched ligand is likely due to steric hindrance for complexation caused by bulky pentyl groups.

Conclusions

Novel hyperbranched polymeric ligands have been synthesized by the modification of polyglycidol and used to catalyze the oxidative coupling terminal acetylenes. A comparison between hyperbranched and low molecular weight analogous reveals definite performance improvement when using hyperbranched amines, however not to the extent of the best ligand known, TMDA. The performance improvement for the case of hyperbranched ligands is likely due to two factors. The first is better complexation abilities and the second is the local increase of reagent concentration. We are working currently on the modifying of hyperbranched ligand structure to further improve their performance in oxidative coupling reaction.

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References

1. Flory P, (1952) Am. Chem. Soc., 74: 2718.
2. Knapen JWJ, van der Made AW, de Wilde JC, van Leeuwen PWNM, Wijkens P, Grove DM, van Koten G. (1994) Nature, 372:659.
3. Hoare JL, Lorenz K, Hovestad NJ, Smeets WJJ, Spek AL, Canty AJ, Frey H, van Koten G. (1997) Organometallics, 16:4167.
4. Bhyrappa P, Young JK, Moore JS, Suslick KS. (1996) J Am Chem Soc, 118:5708.
5. Reetz MT, Lohmer G, Schwickardi R. (1997) Angew Chem, Int Ed Engl 36:1526.
6. Zhao M, Crooks RM. (1999) Angew Chem, Int Ed, 38:364.
7. Mak CC, Chow H-F. (1997) Macromolecules 30:1228.
8. Lee J-J, Ford WT, Moore JA, Li Y. (1994) Macromolecules 27:4632.
9. Marquardt T, LuÈning U. (1997) Chem Commun 1681.
10. Suh J, Hah SS, Lee SH. Bio Chem 1997;25:63.
11. Wegner G, (1970) Makromol Chem, 134:219.
12. Kuhling S, Keul H, and Hocker H, (1990) Macromolecules 23:4192
13. Rong-Chang Liang, Reiser A, (1987) J. Polym. Sci A 25:451.
14. Rubner M, (1986) Macromolecules, 19:2129.
15. Kwock E, Baird T Jr, Miller T, (1993) 26:2935
16. Fomine S, Ogawa T, (1994) Polymer J. 26:95.
17. Fomin S, Neyra R, Ogawa T, (1994) Polymer J. 26:845.
18. Sunder A, Hanselmann R, Frey H, and Mulhaupt R, (1999) Macromolecules , 32:4240.
19 Jaguar 3.5, Schrodinger, Inc., Portland, Oregon, 1998

20. Becke AD, (1988) Phys. Rev. A, 38:3098.
21 Perdew JP, (1986) Phys. Rev. B, 33:8822.
22. Holter D, Burgath A, Frey H, (1997) Acta Polym. 48:30.
23. Sladkov A, Golding I (1979) Russ. Chem. Rev. (Engl Transl), 48:868.
24. Klebanskii A, Grachev I, Kuznetsova O, (1957) J. Org. Chem (Russian) 27:2977.