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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 12 February 2010

To cite this Article El-Hamshary, Hany , Al-Sigeny, Samia and Ibrahim, Mohamed M.(2010) 'Catalytic Activity of Polymer Anchored Cu-tren Complex in the Oxidation of 2,6-Di-*t*-butyl Phenol', *Journal of Macromolecular Science, Part A*, 47: 4, 329 – 334

To link to this Article: DOI: 10.1080/10601320903539249

URL: <http://dx.doi.org/10.1080/10601320903539249>

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Catalytic Activity of Polymer Anchored Cu-tren Complex in the Oxidation of 2,6-Di-*t*-butyl Phenol

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Received June 2009, Accepted September 2009

Poly(styrene-*co*-dimethylaminoethyl methacrylate) and poly(methyl methacrylate-*co*- dimethylaminoethyl methacrylate) were prepared by solution polymerization. These polymers were quaternized by methyl iodide and *n*-hexyl bromide. The produced polymers were used as support in the aqueous oxidation of 2,6-di-*tert*-butylphenol (DBP) using hydrogen peroxide catalyzed by tris(2-aminoethyl)amine copper(II) complex “Cu(II)-tren complex” anchored on the prepared polymers. The products obtained from the reactions were 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone (DPQ) and 2,6-di-*tert*-butyl-*p*-benzoquinone (BQ). No reaction products were obtained when the reaction was carried out in the absence of polymeric catalyst. The polymer composition and reaction medium greatly affect product distribution of the reaction. Polar organic solvent like DMF and methanol favor the formation of DPQ, while nonpolar organic solvent like benzene and methylene chloride favor the formation of BQ. Hydrophobic branches of polymers **6** (PS-HexBr-Cu-TREN) and **8** (PMMA-HexBr-Cu-TREN) favor BQ formation as the weight of support increased. On the other hand, DPQ is favored in the presence of hydrophilic branches as observed for both polymeric catalysts **5** (PS-MeI-Cu-TREN) and **7** (PMMA-MeI-Cu-TREN).

Keywords: Polymeric support, catalytic oxidation, hindered phenols, Cu-complex, product distribution

1 Introduction

Oxidation of hindered phenols is of considerable industrial and synthetic importance as well as environmental priority since they are considered as major water and soil pollutants, in addition to their wide use as stabilizers of oxidation processes (1,2). Oxidation of phenols can be accomplished with many oxidants (3-8). The reaction products are highly sensitive to the reaction conditions. In the absence of any catalyst, the oxidation of hindered phenols results in the formation of a mixture of products (9,10). In catalytic phenol oxidation, the presence and nature of *ortho*-groups on the phenol-ring greatly influence the reactivity. Phenol or mono-substituted derivatives thereof yield branched products, while two small *ortho*-groups tend to favor polymerization. Larger substituents shift the selectivity towards the formation of diphenoquinone (DPQ) (10).

Functionalized polymers and polymer metal complexes were prepared and used to promote a wide range of organic transformation with good catalytic activity, selectivity and reproducibility (11). Heteropolyacids and polymer-

anchored molybdenyl and vanadyl complexes have been used in the oxidation of substituted phenols with *tert*-butylhydroperoxide and H₂O₂ (12-15). We have observed that the reaction products of 2,6-dibutyl phenol and 2,6-dimethyl phenol can be controlled by proper adjustment of reaction conditions as the type of polymeric support, concentration of oxidant, pH, and type of metal catalyst (6, 16). Among the widely used catalysts for the oxidation of hindered phenols are the copper amine complexes (17-21). Copper complexes are attracting attention as models for intermediates in copper enzymes (22-26). Furthermore, the copper-catalyzed phenol coupling used to arrive at chiral biphenol derivatives is used extensively as a test reaction for the catalytic activity of new copper complexes (23).

In this work, we report some studies on the role of polymer structure and other reaction parameters like solvent effect, catalyst amount and phenol concentration in the variation of product ratio in the oxidation of 2,6-di-*tert*-butylphenol (DBP) with hydrogen peroxide as oxidant, catalyzed by copper amine complex: tris(2-aminoethyl)amine copper(II) complex “Cu(II)-tren” anchored on the prepared polymers. The choice of 2,6-di-*tert*-butylphenol (DBP) was due to its reactivity and structural simplicity (27). Besides, the main products of the oxidation are 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone (DPQ) and 2,6-di-*tert*-butylbenzoquinone (BQ) are highly sensitive to the reaction

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conditions, but they have the advantage that they can be easily monitored by conventional analytical techniques (28).

2 Experimental

2.1 Materials

Styrene and methyl methacrylate (Aldrich) were purified by distillation under reduced pressure before use. Divinyl benzene (DVB) and dimethylaminoethyl methacrylate (DMAEMA) were used as received from Aldrich. 2,6-Di-*tert*-butylphenol (DBP) was recrystallized from *n*-Hexane. Tris(2-aminoethyl)amino copper perchlorat [Cu(tren)(H₂O)](ClO₄)₂ was prepared as described previously (29).

2.2 Measurements

Elemental microanalysis was done at the Central Laboratory of Microanalysis at Cairo University. IR was done at The Central Laboratory of Microanalysis at Tanta University and the IR spectra were recorded from KBr pellets.

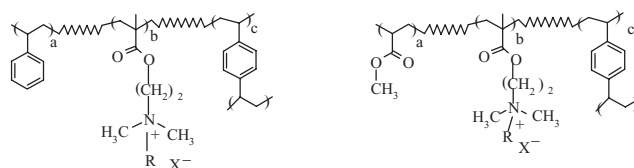
2.3 Polymer Synthesis

Polystyrene-co-DMAEMA: Styrene (7.81 g, 75.0 mol%), DMAEMA (3.93 g, 25 mol %) and DVB (1.0 mol%) were mixed together with cyclohexane (30.0 mL) and purged with nitrogen for 15 min. A solution of benzoyl peroxide (1 wt% based on weights of monomers) was then added and the reaction mixture was heated at 80°C for 20 h. The produced polymer was filtered and washed thoroughly with methylene chloride. The polymer was dried in vacuum at room temperature for 24 h to give 7.2 g. Elemental analysis of the nitrogen content indicated 0.76% of N (yield 25.8%). IR spectra (KBr) showed absorptions at 3340 cm⁻¹ (C=O overtone stretch), 1645 cm⁻¹ (C=O ester), 1590 cm⁻¹ (C–N stretch overlap), and at 2920 cm⁻¹ (CH₂ chain).

On the other hand, polymethyl methacrylate-co-DMAEMA was polymerized using the above procedure and the ratios of monomers to give 7.6 g with 0.95% of N (yield 31.4%). IR spectra (KBr) showed absorptions at 3340 cm⁻¹ (NH amide), 1645 cm⁻¹ (C=O ester), 1590 cm⁻¹ (C–N stretch overlap), and at 2920 cm⁻¹ (CH₂ chain). The produced copolymers were quaternized using methyl iodide and *n*-hexyl bromide (Scheme 1) according to previously published procedure (30). The halide ion content was determined by using Volhard method (31) to give: polymer 1 (PS-MeI) 0.446 mmol I-/g, polymer 2 (PS-HxBr) 0.536 mmol Br-/g, polymer 3 (PMMA-MeI) 0.357 mmol I-/g and polymer 4 (PMMA-HxBr) 0.626 mmol Br-/g.

2.4 Catalyst Preparation

The polymeric catalyst was prepared by the dropwise addition of aqueous Cu-tren solution with magnetic stirring to



1 : PS-MeI
RX = CH₃-I

5 : PS-MeI-Cu-TREN

2 : PS-HexBr
RX = CH₃-(CH₂)₅-Br

6 : PS-HexBr-Cu-TREN

3 : PMMA-MeI
RX = CH₃-I

7 : PMMA-MeI-Cu-TREN

4 : PMMA-HexBr
RX = CH₃-(CH₂)₅-Br

8 : PMMA-HexBr-Cu-TREN

Catalyst = [Cu(II) (TREN) H₂O] (ClO₄)₂

TREN = N(CH₂-CH₂-NH₂)₃

Sch. 1. Catalyst Preparation.

a suspension of the polymer. The copolymer Cu-tren complex was stirred for about 4 h and then filtered and washed with deionized water and dried in vacuum. The amount of Cu-tren 'bound' was determined by reacting the polymer complex with standard HCl and the liberated Cu^{II} was determined by titration using standard EDTA solution.

2.5 Oxidation of 2,6-DTB

In a typical experiment; the polymeric Cu-tren catalyst previously prepared was finely ground and added to 40 mL H₂O placed in 100-mL glass reactor with magnetic stirring for 30 min. The polymeric catalyst is easily dispersed in water and forms stable slurry. The pH was adjusted to 9.0 by addition of 5 mL of 0.1 M borate buffer, no salt was added to adjust ionic strength. A solution of phenol (3.0 mmol) dissolved in 2.50 mL of methanol was then added. The reaction was started by injecting 3 mmol of H₂O₂ (30% aqueous solution) where the total reaction volume was maintained at 50.0 mL. The reactions were run for 4 h at 40°C under air. At the end of the reaction, the solid polymer was filtered off, and washed with methylene chloride. The organic products were extracted from the filtrate by methylene chloride (3 × 25 mL). The combined extracts and the washing were dried over anhydrous magnesium sulfate and evaporated under vacuum. The products formed were separated by preparative layer chromatography GF₂₅₄ (solid phase-silica gel plates 2 mm thickness, eluent petroleum ether: ethyl acetate 9.5: 0.5). The reaction products were identified by elemental microanalysis and IR spectra, melting points and by comparison with authentic samples. The products formed were (a) 2,6-di-*tert*-butylbenzoquinone (BQ) and (b) 3,3',5,5'-tetra-*tert*-butyldiphenquinone (DPQ).

A blank catalytic oxidation experiment was carried out in the absence of catalyst and polymeric support. Another blank experiment was carried out using the polymeric materials PS-MeI and PS-HxBr, but without Cu-tren.

Table 1. The composition of copolymers and yield and other details for the synthesis

Samples	Composition (mol %)		^a X mmol/g (X = I, or Br)		Cu % mmol/g
	Styrene	DMAEMA	Found	Calcd	
5 (PS-MeI-Cu-tren)	75	25	0.446	2.17	0.244
6 (PS-HxBr-Cu-tren)	75	25	0.536	1.51	0.389
Samples	Composition (mol %)		^a X mmol/g (X = I, or Br)		Cu % mmol/g
	MMA	DMAEMA	Found	Calcd	
7 (PMMA-MeI-Cu-tren)	75	25	0.357	1.74	0.313
8 (PMMA-HxBr-Cu-tren)	75	25	0.626	2.72	0.427

^aX = I⁻ in samples 5 and 7; and Br⁻ in samples 6 and 8.

3 Results and Discussion

Polymeric supports with different chemical structure have been synthesized in order to study the product distribution of 2,6-DBP since the products of hindered phenols are highly sensitive to the reaction medium. Two copolymers based on styrene and on methyl methacrylate (MMA) were prepared using 1 mol% of the crosslinker DVB and the functional monomer dimethylaminoethyl methacrylate (DMAEMA) 25 mol%. The ratio of styrene/DMAEM and MMA/DMAEM was 3:1. Polymers were prepared by a free radical solution polymerization of the monomers in cyclohexanone at 80°C for 20 h using benzoyl peroxide as initiator. The produced copolymers were then quaternized with two different alkyl halides having different chain length; methyl iodide, and n-hexyl bromide (Scheme 1) to give polymeric salts **5–8** with low conversion ~20–35% to facilitate complex formation with copper.

The IR spectrum of the copolymers shows bands due to carbonyl groups at 1645 cm⁻¹ (C=O ester). This band did not change much after complex formation with metal; however, its intensity was lowered due to a low concentration of the complex Cu-TREN on the polymer network. The obtained polymeric salts had varied hydrophile-lipophile nature within the polymer itself. The composition of copolymers, yield, and other details for the synthesis of the chelating resins are given in Table 1.

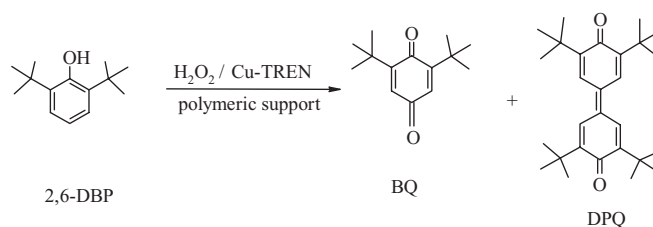
3.1 Catalytic Oxidation

The polymeric salts were used as supports in minute amounts ~0.1 g for Cu-tren catalyst in the aqueous oxidation of 2,6-di-*t*-butylphenol (DBP) using hydrogen peroxide as oxidizing agent. The catalyst was bound to the polymeric support as indicated from changes in IR spectrum and analysis of the bound copper. The molar ratio of H₂O₂ to catalyst was about 10 for polymeric catalysts **5** and **7** and was 7 for polymeric catalysts **6** and **8**. The predominant products formed in the oxidation reactions were 2,6-di-*t*-butyl-*p*-benzoquinone (BQ) and 3,3'-5,5'-tetra-*t*-

butyl-diphenoquinone (DPQ) (Scheme 2). The efficiency of the polymeric catalysts is presented as the percentage of 2,6-DBP conversion and percentage of formation of DPQ and BQ.

Results of the catalytic efficiency and solvent effect for the oxidation of 2,6-DBP with various polymer catalysts using H₂O₂ as oxidant in water and in different solvents are reported in Table 2.

The oxidation of 2,6-DBP with Cu-tren catalyst only in the absence of polymeric support proceeds in very low yield compared to Cu-tren anchored catalysts. In addition, traces of unidentified products were obtained in the case of using polymeric materials PS-MeI but without Cu-tren and nothing with PS-HxBr under the same conditions, which mean that the halide ion content is not enough to oxidize the phenol. From Table 2 it is clear that the observed % conversion of DBP was higher in polar solvent than that in non-polar solvents. DMF was the most efficient solvent for catalytic oxidation of DBP, followed by MeOH, H₂O, CH₂Cl₂, and benzene, respectively. It has been observed that polar solvents such as acetonitrile and methanol gave a higher yield in the oxidation of 2,6-DBP using *t*-BuOOH catalyzed by polymer-anchored molybdenyl and vanadyl complexes and the reaction proceeds via a radical pathway involving phenolato peroxy metal complex intermediate (15). It is also suggested by Sheldon and Kochi (10) that vanadyl and molybdenyl complexes catalyzed oxidation of DBP using *t*-BuOOH preferably by its heterolysis i.e., facilitating the ionizing pathway. These suggestions are in good agreement with what was observed in our system; the increased

**Sch. 2.** Oxidation of 2,6-DBP.

polarity of the solvent facilitated the formation of metal-complexed-phenolato intermediate that results in increasing product yield. Metal complexed phenolate intermediate produced 2,6-di-*tert*-butylbenzoquinone (BQ). The phenoxy radical is produced through the minor pathway of the reaction, metal catalyzed homolytic decomposition of the hydroperoxide. Formation of 3,3'-5,5'-tetra-*tert*-butyl-diphenoquinone (DPQ) can be explained by the coupling of a phenoxy radical with another phenoxy radical (32).

In addition, the polystyrene-based catalysts **5** (PS-MeI-Cu-tren) and **6**; (PS-HxBr-Cu-tren) were more active when compared with polymethyl methacrylate-based catalysts **7**; (PMMA-MeI-Cu-tren) and **8** (PMMA-HxBr-Cu-tren). This could be due to the hydrophobic nature of polystyrene phenyl rings which absorb more substrate molecules through $\pi - \pi$ interaction between the π electrons in the aromatic ring of the phenolic species and π electrons in the copolymer network due to phenyl rings (33), thus making them much closer to the active sites distributed within the polymeric catalyst network, so that the reaction with phenol will be more efficient and, as a result, more phenol molecules react. However, in the case of using H₂O as solvent for both catalysts **6** and **8**, the conversion of DBP was significantly decreased; this is probably due to the re-

duced swelling of the polymeric catalysts in water. Indeed, the equilibrium water uptake of these polymers was found to vary between 5.5 for the poly(styrene) based polymers and 9.1 for poly(methyl methacrylate) based polymers. This results in a decrease in the concentration of the DBP inside the polymeric catalyst and as a result decreases the possibility of interactions between the DBP and H₂O₂. However, when polar organic solvents were used, such as DMF and methanol, this behavior was greatly altered; the amount of substrate substantially increased within the polymer network and their interaction with the active sites distributed through the polymer which led to an increase in phenol conversion. The formation of dibutyl-phenoquinone (DPQ) is favored in polar solvents, while benzoquinone (BQ) formation is favored by nonpolar solvents. It is also observed that the nature of the polymer structure affects the product distribution; the amount of BQ increased as the hydrophilic nature of the polymer structure increased. This effect was further investigated below.

3.2 Amount of Polymer

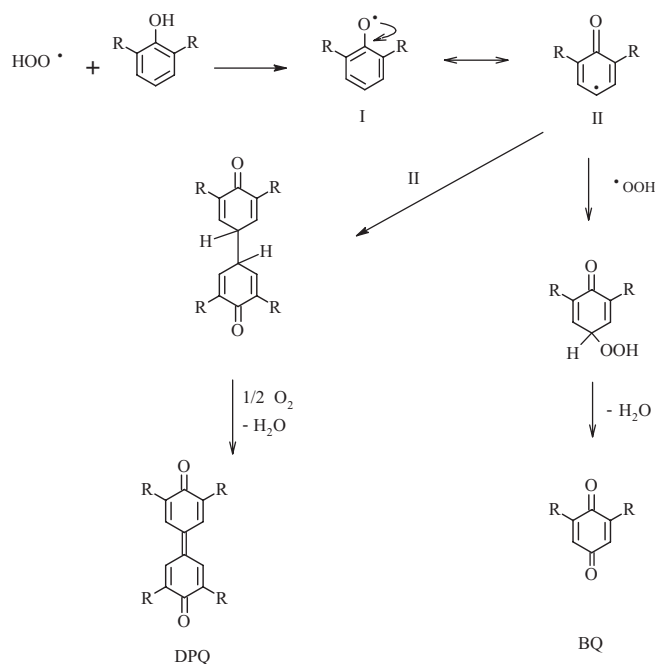
The effect of increasing amounts of polymeric catalyst was studied in water and is presented in Table 3. In fact,

Table 2. Oxidation of 2,6-di-*tert*-butylphenol using different polymeric support

Polymeric support	Solvent	% conversion ^b Of DBP	Product ratio (%) ^b	
			BQ	DPQ
Cu-tren	Water	traces	—	—
PS-MeI	Water	traces	—	—
PS-HexBr	Water	traces	—	—
5 (PS-MeI-Cu-tren)	Water	70	36	64
6 (PS-HexBr-Cu-tren)	Water	30	17	83
7 (PMMA-MeI-Cu-tren)	Water	60	36	64
8 (PMMA-HexBr-Cu-tren)	Water	15	67	33
5 (PS-MeI-Cu-tren)	MeOH	60	33	67
6 (PS-HexBr-Cu-tren)	MeOH	70	43	57
7 (PMMA-MeI-Cu-tren)	MeOH	25	60	40
8 (PMMA-HexBr-Cu-tren)	MeOH	26	77	23
5 (PS-MeI-Cu-tren)	DMF	70	14	86
6 (PS-HexBr-Cu-tren)	DMF	80	19	81
7 (PMMA-MeI-Cu-tren)	DMF	60	33	67
8 (PMMA-HexBr-Cu-tren)	DMF	40	25	75
5 (PS-MeI-Cu-tren)	Benzene	30	83	17
6 (PS-HexBr-Cu-tren)	Benzene	30	67	33
7 (PMMA-MeI-Cu-tren)	Benzene	30	83	17
8 (PMMA-HexBr-Cu-tren)	Benzene	15	67	33
5 (PS-MeI-Cu-tren)	CH ₂ Cl ₂	55	73	27
6 (PS-HexBr-Cu-tren)	CH ₂ Cl ₂	50	50	50
7 (PMMA-MeI-Cu-tren)	CH ₂ Cl ₂	40	75	25
8 (PMMA-HexBr-Cu-tren)	CH ₂ Cl ₂	45	56	44

^aAll reactions were carried out at 40°C with 0.16 g of polymer, 3.0×10^{-2} M of 2,6-DBP, and 6.0×10^{-2} M of H₂O₂. All reactions were carried out in the presence of 5 mL of borate buffer pH 9. The reaction mixture had a volume of 50 mL including 2.50 mL methanol solution of DBP. The reactions were carried out for 4 h.

^bPercent conversion based on isolated products.



R = t-Bu

Sch. 3. Possible mechanism for oxidation of 2,6-di-t-butylphenol.

increasing the amount of polymer relates to increasing the number of mmols of Cu-tren. In general, the percentage of converted phenol increased with increasing the amount of polymer where the number of mmols of Cu-tren active sites available to substrate increased, so that the probabilities of reaction with large number of substrate molecules increased and as a result, the percentage of conversion increased. This trend is observed for all polymeric supports although the percent conversion for both **6** (PS-HxBr-Cu-tren) and **8** (PMMA-HxBr-Cu-tren) is lower than that of **5** (PS-MeI-Cu-tren) and **7** (PMMA-MeI-Cu-tren). What is interesting in this case is the increased yield of BQ derivative for the two supports **6** and **8** as the amount of polymer increased. It appears that the nature and number of the branches of the polymeric support controls the ratios of product distribution; that is long chain hydrophobic branches favor BQ formation as the weight of **6** (PS-HxBr-Cu-tren) and **8** (PMMA-HxBr-Cu-tren) supports an increase, while DPQ is favored in the presence of hydrophilic branches as observed for both **1** (PS-MeI-Cu-tren) and **5** (PMMA-MeI-Cu-tren).

3.3 Amount of Phenol

The effect of increasing the amount of DBP was studied in water and is presented in Table 4. It was found that the percent conversion of DBP decreased as the concentration of phenol increased. We expect that competition due to the presence of a large number of substrate molecules within

Table 3. Oxidation of 2,6-di-tert-butylphenol using different amount of polymers

Polymeric support	[Polymer] ^a	% conversion ^b of DBP	Product ratio (%) ^b	
			BQ	DPQ
5 (PS-MeI-Cu-tren)	0.16	70	36	64
	0.37	80	25	75
	0.53	85	14	86
	0.81	90	5	95
6 (PS-HexBr-Cu-tren)	0.16	30	17	83
	0.37	35	57	43
	0.53	40	75	25
	0.81	50	90	10
7 (PMMA-MeI-Cu-tren)	0.16	60	63	37
	0.37	55	36	64
	0.53	65	38	62
	0.81	75	20	80
8 (PMMA-HexBr-Cu-tren)	0.16	15	67	33
	0.37	25	60	40
	0.53	30	67	33
	0.81	40	87	13

^aAmount of polymer in grams. ^bPercent conversion based on isolated products. Other reaction conditions are listed under Table 2.

the polymeric network decreases the possibility of reaction with catalyst active sites accessible to the substrate molecules. As the amount of DBP increased to the weight of support, the amount of BQ formed was more than that

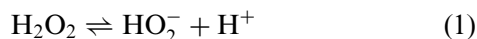
Table 4. Oxidation of 2,6-di-tert-butylphenol using different concentrations of phenol

Polymeric support	[phenol] ^a	% conversion ^b of DBP	Product ratio (%) ^b	
			BQ	DPQ
5 (PS-MeI-Cu-tren)	0.375	95	8	92
	0.75	78	21	79
	1.50	70	35	65
	3.00	50	60	40
6 (PS-HexBr-Cu-tren)	0.375	60	12	88
	0.75	50	17	83
	1.50	30	20	80
	3.0	25	25	75
7 (PMMA-MeI-Cu-tren)	0.375	90	2	98
	0.75	85	6	94
	1.50	75	11	89
	3.00	60	17	83
8 (PMMA-HexBr-Cu-tren)	0.375	70	31	69
	0.75	60	35	65
	1.50	40	38	62
	3.00	20	75	25

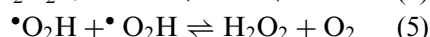
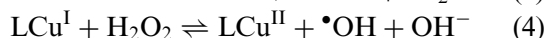
^aAmount of DBP in mmol, ^bPercent conversion based on isolated products. Other reaction conditions are listed under Table 2.

of DPQ as observed previously for the effect of amount of polymer (Table 4).

Now a possible mechanism of the reaction of Cu-tren (let us say LCu^{II}) with H₂O₂ could be proposed to proceed as follows:



Then, the association of anion HO₂⁻ with LCu^{II} yielded LCu^{II}-OOH⁻, which subsequently produces peroxy radical (34–36), as follows; reaction 3:



The peroxy radical reacts with DBP [1a, 1b] to give products as follows:

Polar solvents favor C-C coupling which lead to formation of DPQ, while nonpolar solvents favor C-O coupling that lead BQ [1b]. However, the influence of the solvent is also affected by the polymer structures hydrophilic branches favor DPQ, while BQ is favored in the presence of hydrophobic branches.

3.4 Conclusions

The results show that careful choice and proper adjustment of the polymer composition and reaction medium greatly affect the reaction products. In the present catalytic systems, hydrophobic branches favor BQ formation as the weight of support increased **6** (PS-HxBr-Cu-tren) and **8** (PMMA-HxBr-Cu-tren); while DPQ is favored in the presence of hydrophilic branches as observed for both **5** (PS-MeI-Cu-tren) and **7** (PMMA-MeI-Cu-tren). Polar organic solvent like DMF and methanol favor the formation of DPQ, while nonpolar organic solvent like benzene and methylene chloride favor the formation of BQ. The percent conversion of DBP decreases as the amount of substrate increase. Careful choice of the polymeric support – catalyst system and reaction medium can be used to control the product distribution of industrial valuable specific substrate.

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