The Consequences of Surface Confinement on Free Radical Chemistry

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ABSTRACT

Mass transport limitations impact the thermochemical processing of fossil and renewable energy resources, which involves the breakdown of cross-linked, macromolecular networks. To Investigate the molecular level details of the consequences of molecular confinement on high temperature $(275-500\,^\circ C)$ free-radical reaction pathways, we have been examining the pyrolysis of model compounds attached to the surface of non-porous silica nanoparticles through a thermally robust Si-O-C$_{aryl}$ tether. Pyrolysis of silica-immobilized diphenylalkanes and related ethers have been studied in detail and compared with the corresponding behavior in fluid phases. The diffusional constraints can lead to reduced rates of radical termination on the surface, and enhancement of neophyl-like rearrangements, cyclization-dehydrogenation pathways, and ipso- aromatic substitutions. Furthermore, studies of two-component surfaces have revealed the importance of a radical relay mechanism involving rapid serial hydrogen transfer steps resulting from the molecular pre-organization on the low fractal dimension silica surface. Key findings are reviewed in this paper, and the implications of these results for fuel processing are described.

INTRODUCTION

Pyrolysis forma the basis for many current and envisioned technologically important processes for conversion of fossil and renewable resources into volatile fuels or chemicals. Since many of these resources are highly cross-linked, macromolecular organic materials. concerns over mass transport limitations are often well-founded. The effects of mass transport limitations have been documented in the pyrolysis of coal,[1] kerogen,[2] cellulose,[3] lignin,[4] biomass,[5] and polymers." Predictive models have been developed for pyrolysis of coal, lignin, and cellulose that explicitly include descriptions of mass transport mechanisms.[1b-d] These mass transport limitations can impact pyrolysis rates, and govern the tar yields and molecular weight distributions.

Our knowledge of the effects of mass transport is primarily on a macro scale, e g. lumped kinetic parameters and product classes. Pyrolysis studies on complex materials such as coal do not yield direct information about the *individual* chemical processes that control reaction rates, or about the actual molecules that are responsible for formation of particular products. An enhanced understanding of the effects of mass transport limitations on pyrolysis reactions *at a molecular level has been* a goal of our research. Hence, we have been exploring the pyrolysis chemistry of organic molecules that serve as models for constituents in biopolymers and geopolymers: Restricted mass transport conditions have been simulated by confuting these molecules to the surface of nonporous silica nanoparticles through a covalent linkage. Many of the manifestations of mass transport limitations on high temperature organic reactions involving free-radical intermediates are now much better understood as a consequence of our extensive studies on these silica-immobilized model compounds. A brief overview of key findings from our studies of hydrocarbon pyrolysis will be presented. and a more detailed review of this work is in press."

PREPARATION OF SILICA-IMMOBILIZED MODEL COMPOUNDS

In selection of a surface-immobilization technmque for our investigauons of the pyrolysis mechanisms, we were guided by several cntena. Both the support and linkage must be stable at the temperature regime of interest, up to ca. $450-500\,^\circ C$. The support should have a moderately high surface area with enough accessible active sites for attaching significant quantities of the organic molecules of interest Any unreacted sites should not be catalytically active, e g. Bronsted or Lewis acid sues. The position of surface attachment within the organic moiety should be far enough removed from the normal position of thermal reactivity so as not to induce significant substituent effects For flexibility, the organic functional group used in the attachment should be readily synthesized. Finally, a very important criterion arises from our desire to be able to identify and

quantitate all pyrolysis products, both in the gas phase and those that remain attached to the surface of the support. Namely. although the covalent link should be thermally stable, there must exist a facile chemical method for cleaving products from the surface for analysis. To meet all these requirements, we chose the reaction of substituted phenols with the silanols of a high purity, nonporous fumed silica (Cabosil M-5. 200 m^2 g^{-1}, ca. 4 5 SiOH nm^{-2} or 1 5 mmol SiOH g^{-1}) as shown in Figure 1.[8-10]

Surface coverages can be varied (typical range of 0 06 - 0 6 mmol g^{-1}) by adjusting the initial phenol to surface hydroxyl ratio, and saturated surface coverages are obtained by using excess phenol. Unreacted phenol is removed either by sublimation under vacuum at ca 270°C or by Soxhlet extraction with a solvent like benzene. The silicon-oxygen-aromatic carbon linkage, Si-O-C,,. has been found to be thermally robust up to at least 450°C [8-11] However. the linkage is hydrolytically unstable under aqueous base conditions. This allows us to detach pyrolysis products from the silica surface as the corresponding phenols, as well as any unreacted starting material, for identification and quantitation. This important advantage for our pyrolysis studies also represents a potential limitation for this linkage if reaction studies in aqueous or nucleophilic solvents are of interest. Another limitation of this method is ambiguity in the point of attachment to the surface if a second active functional group (alcohol. thiol, etc.) is present in the molecule. Surfaces can also be prepared with two point attachment of the model compound (Figure 1),[12] although high efficiencies for di-attachment (SO-90 %) occur only at rather low surface coverages (ca 0 1 mmol g^{-1}). We have also found that a variety of two-component surfaces are easily prepared by co-attachment of the molecules to the silica in a single step.[14-16]

PYROLYSIS STUDIES

The surface-attached diphenylalkanes, ≈C$_6$H$_4$(CH$_2$)$_n$C$_6$H$_5$ [n=0-4], have been prepared and used as models for aliphatic bridges between aromatic molecules in fossil fuels.[8-12] The "≈" notation is employed as an abbreviation to represent the Si-O-C, linkage to the silica surface, In addition, analogs such as ≈C$_6$H$_4$XCH$_2$C$_6$H$_5$ [X = O,[15] S[16]],≈C$_6$H$_4$OCH$_2$CH$_2$C$_6$H$_5$,[17,18] and ≈C$_6$H$_4$CH$_2$CH$_2$OC$_6$H$_5$[17,18] have been recently examined to explore the important effects of heteroatoms. The pyrolysis behavior of surface-immobilized compounds have been thoroughly examined as a function of reaction extent, temperature, surface coverage, and degree of cross linking,[8-10,12] as well as the presence of a hydrogen atmosphere,[14,19] a second co-attached molecule of variable structure,[10,13,14] and a solid-state acid[20] or hydrogenation catalyst.[19] The reaction kinetics, mechanisms. and product selectivities have been compared with that of the corresponding molecules in fluid phases. Due to space limitations, only a few of the major findings will be surveyed below with an emphasis on free radical chemistry

Vacuum pyrolysis reactions were typically performed in sealed T-shaped Pyrex tubes in a temperature controlled (± 1 °C) tube furnace. Volatile products were collected in the side arm trap cooled with liquid nitrogen, while surface-attached products were recovered as the corresponding phenols following basic digestion of the silica. The products were identified and quantitated principally by GC and GC-MS with the use of authentic reference materials and internal calibration standards.

≈C$_6$H$_4$(CH$_2$)$_n$C$_6$H$_5$ [n=0,1]. Biphenyl contains only strong bonds that are stable at 400°C. Likewise, we found that the surface-immobilized form, ≈Ph-Ph, was stable at 400°C for many hours.[8] This indicates that the silica surface and residual silanol groups did not induce any new reaction pathways. Similarly, surface-immobilized diphenylmethane was also found to be stable at 375-400°C.[9] This structure would be quite susceptible to acid-catalyzed cracking reactions,[20] and their absence is further testament to the inert nature of the fumed silica surface. At higher temperatures (425-450°C), we have recently observed a slow reaction involving a competing cyclization pathway and a previously undetected radical Ipso-substitution pathway involving ≈C$_6$H$_4$CH•C$_6$H$_5$ as shown in Figure 2.[21] The radical substitution path appears to be promoted by the diffusional constraints, and the selectivity for this path is currently being studied in more detail.

≈C$_6$H$_4$XCH$_2$C$_6$H$_5$ [X = CH$_2$, O, S]. These model compounds represent structures containing weak bridges between aromatic rings that cleave at T ≤ 400°C as shown in Eq. I

$$\approx C_6H_4XCH_2C_6H_5 \; \rightarrow \; \approx C_6H_4X\bullet \; + \; C_6H_5CH_2\bullet \qquad (1)$$
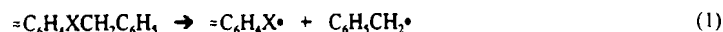
The rate constants and activation parameters measured for X = CH$_2$[8] and O[15] at high surface coverages are similar to those reported for fluid-phase analogs, indicating that the unimolecular homolysis steps are not affected by the surface attachment. However, we find that the product distributions are substantially Impacted. This is illustrated in Figure 3 for the case of silica-attached 1,2-diphenylethane or bibenzyl. The formation of comparable amounts of surface-attached and gas-phase toluene products demonstrates a general finding that there is enough conformational freedom on the surface to permit oriented hydrogen transfers between surface-bound molecules and surface-bound free radicals. However. restricted diffusion retards the rates of radical termination on the surface through bimolecular coupling of intermediate radicals such as ≈C$_6$H$_4$XCH•C$_6$H$_5$ As shown

in Figure 3 for the case of bibenzyl, this eliminates the formation of a major product (tetraphenylbutanes) found in fluid phases. As a consequence, new pathways emerge in significant quantities such as cyclization-dehydrogenation (establishing the phenanthrene skeleton for $X = CH_2$, but not detected for $X = O,S$) and skeletal rearrangements. In particular, neophyl-like rearrangements involving 1,2-phenyl shifts have been found to be important for all cases (Eq 2).[8,15,16] The efficiency of the rearrangement path has been found to depend strongly on the

$$\approx C_6H_4XCH \bullet C_6H_5 \;\; \rightleftharpoons \;\; \approx C_6H_4(C_6H_5)CHX \bullet \qquad\qquad (2)$$
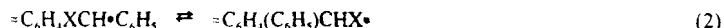
surrounding environment on the surface. Neighboring hydrogen sources are needed to trap the typically less stable rearranged radical. Hence, a low surface coverage of bibenzyl or the presence of neighboring aromatic spacer molecules (such as naphthalene) inhibits this rearrangement path.[22] Conversely, this path is prominent at high bibenzyl surface coverages or in the presence of neighboring molecules that can donate hydrogen (such as diphenylmethane). The resulting hydrogen transfer, radical relay path is important in overcoming some of the effects of diffusional constraints, and has been studied in detail in the pyrolysis of 1,3-diphenylpropane as discussed below. It is important to note that, for bibenzyl, this process is a retrograde pathway that generates a more refractive diphenylmethane linkage. For the benzyl phenyl ether analog, new reactive products (benzophenone and benzhydrol) are generated that were not previously reported in fluid phases. In the benzyl phenyl sulfide case, the rearranged product, $\approx C_6H_4(C_6H_5)CHSH$, is particularly unstable and reacts further to form surface-attached diphenylmethane.

Because of the significance of this rearrangement path under restricted mass transport conditions, the pyrolysis of immobilized bibenzyl has been investigated in several different environments. We recently found that a co-attached hydrogen donor, tetralin, is ineffective at retarding the rearrangement path.[22] The impact of hydrogen pressure on this pathway was also studied through pyrolysis of $\approx BB$ at 400°C in a high pressure reactor in the presence of a nitrogen or deuterium atmosphere (14 MPa).[19] Pyrolysis under D_2 produced the expected higher yields of hydrocracked products such as $\approx C_6H_4D$ and $C_6H_5CH_2CH_2D$, as well as lower yields of alkene products, compared with pyrolysis under N_2 or vacuum. However, D_2 pressure was unable to prevent the retrogressive rearrangement pathway (or the cyclization pathway) from occurring under the diffusional constraints. A similar result was also obtained for a different type of silica-immobilized bibenzyl under D_2, which was prepared by attachment of a carboxylic acid derivative to silica via a $SiO^- - Ca^{2+} - {^-}O_2CPhCH_2CH_2Ph$ ionic linkage.[23]

$\approx C_6H_4CH_2CH_2XC_6H_5 (X = CH_2, O)$. 1,3-Diphenylpropane (DPP) has been employed as a model for longer linkages between aromatic clusters in coal that decay at significant rates at 350-400°C by a free radical chain mechanism as shown in Figure 4. Our studies of silica-immobilized DPP showed that this type of linkage also decayed efficiently in this temperature regime under conditions of restricted mass transport, but pyrolysis rates were extremely sensitive to surface coverage and the structure of neighboring molecules on the surface.[8,9] As shown in Table I, the rate of decomposition of $\approx DPP$ decreased dramatically with decreases in surface coverage as the rate of the bimolecular hydrogen transfer steps decrease. In particular, hydrogen transfer between two surface bound species (Figure 4. Insert) would be particularly affected by increasing spatial separation on the surface. These effects were amplified when DPP was further restrained by having both ends of the molecule tethered to the surface.[12] At a surface coverage of 0.1 mmol g^{-1}, the pyrolysis rate decreased by an additional factor of 4-7 for the two =DPP= isomers studied, for which about 80 % of the molecules were di-attached with the remainder being mono-attached.

The rate of pyrolysis of =DPP at 375°C spanned a remarkably wide range (830-fold), as shown in Table I, and was very sensitive to the structure of neighboring spacer molecules on the surface. When compared at similar low surface coverages of $\approx DPP$ (ca. 0.10-0.14 mmol g^{-1}), aromatic spacer molecules such as biphenyl and naphthalene had little effect on the pyrolysis rate. However, spacer molecules containing benzylic C-H bonds, such as dimethylbenzene, diphenylmethane, tetralin, and fluorene, acted as catalysts to accelerate the decomposition of $\approx DPP$, and the decomposition rates correlated with reported relative rates for hydrogen donation of these molecules to benzylic radicals.[8,9] This behavior is unique to the diffusionally constrained system, since in fluid phases, these molecules behaved like other inert aromatic diluents. This unexpected behavior could be explained by a hydrogen transfer, radical relay mechanism on the surface as illustrated in Figure 5 for the diphenylmethane spacer. Rapid serial hydrogen transfer steps can occur on the surface since the reacting species are pre-organized for reaction in this reduced dimensional reaction space. The involvement of these hydrogen transfer steps for the diphenylmethane spacer were confirmed through isotopic labeling studies with $\approx PhCD_2Ph$ as spacer.[14] As shown in Table I, a full kinetic isotope effect of 2.8 was detected at 375 °C for $\approx$ DPP pyrolysis, and deuterium was incorporated in both the vapor-phase and surface-attached toluene products. The significance of this omnipresent process is that radical centers can migrate by a non-diffusional pathway that overcomes some of the diffusional constraints and promotes the radical chain decomposition pathway. However, as noted earlier, retrogressive reactions for weak cross links as typified by $\approx$ BB are also limited by

hydrogen transfer steps and are promoted by neighboring molecules that can participate in the radical relay mechanism

Undoubtedly, the efficiency of this pathway also depends on the ability of molecules to become properly aligned for the oriented hydrogen transfer step on the surface. an area that needs to be studied in more detail Orientation effects can lead to regiospecificity in hydrogen transfer steps that impact product selectivities. This is illustrated in the pyrolysis of =DPP where hydrogen abstraction selectivities (Figure I) varied modestly with changes in surface coverage, favoring abstraction From the benzylic methylene farthest from the surface at lower surface coverages. More dramatic effects on product selectivities were found during pyrolysis of surface-immobilized 1,4-diphenylbutane where radical chain decomposition products are formed from both benzylic and non-benzylic carbon-centered radicals as described previously [10] Once again, the presence of neighboring molecules that block or promote hydrogen transfer steps significantly alter product selectivities

We have also been investigating ether analogs such as silica-attached phenethyl phenyl ether, $\approx C_6H_4CH_2CH_2OC_6H_5$ ($\approx$PPE), which are models for important structural elements in lignin. [17 18] Pyrolysis at 375°C follows a similar course to that observed in fluid phases. Analogous to diphenylpropane, a radical chain pathway is observed that cycles through the benzylic radical, $\approx C_6H_4CH\cdot CH_2OC_6H_5$, producing phenol and surface-attached styrene products. However, for $\approx$ PPE, a second significant reaction pathway is detected that proceeds through the non-benzylic radical, $\approx C_6H_4CH_2CH\cdot OC_6H_5$. As in the case of benzyl phenyl ether (see Eq. 2), this radical undergoes an oxygen to carbon phenyl shift resulting (following β-scission and H-abstraction) in the formation of benzaldehyde and surface-attached toluene. [17] This pathway is significant for a number of substituted PPE's, but the selectivity is sensitive to substituent effects in a predictable manner. However, as opposed to fluid phases where dilution of PPE with biphenyl solvent had no effect of the selectivity of the two radical decay paths, the rearrangement path involving the O-C phenyl shift was recently found to be sensitive to the structure of neighboring spacer molecules on the silica surface. [17] Aromatic spacers molecules such as biphenyl appear to hinder the O-C phenyl shift, presumably by steric interference. These spacer effects continue to be investigated.

SUMMARY

Restricted mass transport has been recognized as playing an important role in the pyrolysis of cross-linked, macromolecular systems. A molecular level understanding of the impact of diffusional constraints on pyrolysis mechanisms is crucial to bench marking results from analytical pyrolysis experiments, and could be important io developing more refined predictive models for the pyrolysis of fossil and renewable organic energy resources. Model systems that incorporate diffusional constraints such as polymers and covalently or ionically immobilized compounds can provide some of this needed information. Through our studies of silica-immobilized hydrocarbons, we have obtained comprehensive information on how pyrolysis rates and product distributions can be perturbed by restricted mass transport. In general, the rates of unimolecular homolyses are little perturbed by surface immobilization. However, termination reactions between diffusionally constrained radicals are hindered, particularly coupling reactions. This often results in the emergence of competitive radical chain pathways involving unimolecular steps such as skeletal rearrangements and cyclizations. Furthermore, hydrogen transfer processes between diffusionally constrained species cart be particularly facile, although quite dependent on the distance between and the orientation of, the participating species. Under optimum hydrogen transfer conditions, rapid serial hydrogen transfers can occur and provide a means for radical sites to be translocated in the matrix without the need for physical diffusion. Such a process promotes radical chain reactions that can produce smaller, more volatile products, as well as retrogressive reactions that produce more refractory products.

ACKNOWLEDGMENTS

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Table 1. Pyrolysis of Silica-Immobilized $Ph(CH_2)_3Ph$ at 375°C   Influence of Surface Composition on Pyrolysis Rate

Surface Composition[a]	Coverage (mmol g^{-1})	Rate 10^{-4} (% $^{-1}$)[b]	Ref.
≈DPP	0.59	24	9
	0 14	1.1	9
	0. IO	0 72	13
=DPP= (p-,p-)	0 IO	0.17	12
≈DPP≈ (m-p-)	0 09	0 IO	12
≈DPP / ≈BP	0 13 / 0.51	2 2	14
=DPP I =NAP	0 12 / 0.44	1.9	14
≈DPP / ≈DMB (3,4-)	0 12 / 0.25	8 5	14
=DPP / ≈DPM	0.14 / 0.41	37	14
≈ DPP / ≈DPM-d_2	0 12 / 0.35	13	14
=DPP / ≈TET	0 II 1045	47	25
≈DPP / ≈FL	0 17 IO.42	83	14

[a] Abbreviations for surface-attached species are ≈DPP (1,3-diphenylpropane, mono-attached), ≈DPP≈ (DPP, 80 % di-attached. 20 % mono-attached). ≈BP (biphenyl), ≈NAP (naphthalene), ≈DMB (dimethylbenzene), ≈DPM (diphenylmethane), ≈DPM-d_2 (PhCD$_2$Ph), ≈TET (tetralin), ≈FL (fluorene) [b] Initial rates for total decomposition of DPP based on 4-8 thermolyses. Standard deviations (1σ) in reported values are typically ≤15%.
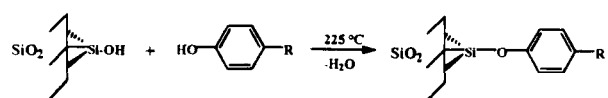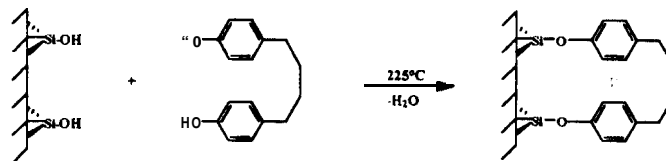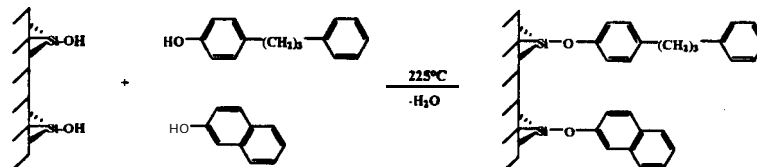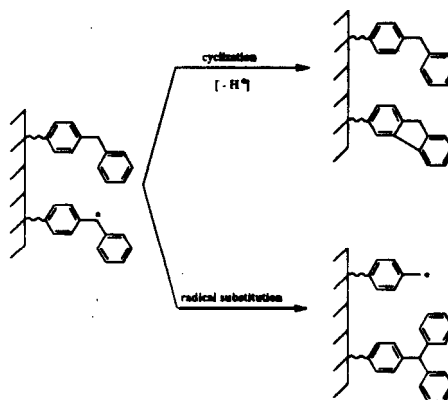
Figure **1.** Preparation of silica-immobilized model compounds

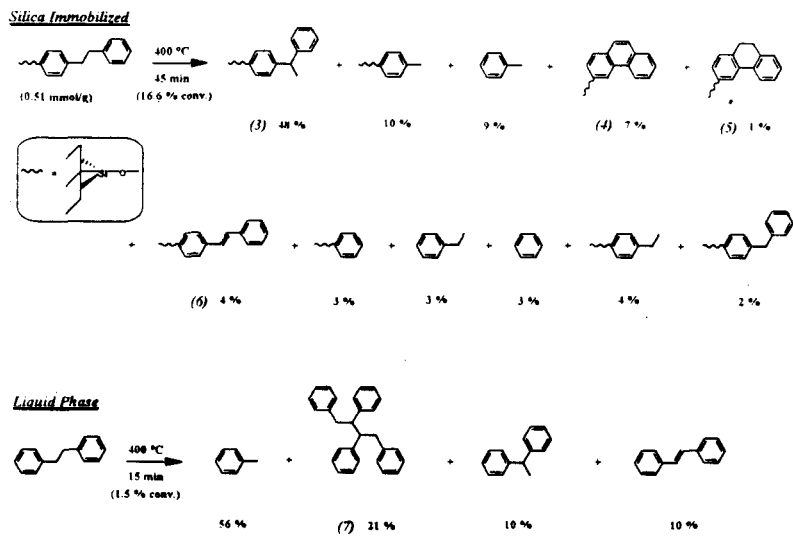Figure 2. Competing cyclization and radical substitution pathways in pyrolysis of sdica-immobilized diphenylmethane.

Figure 3. Comparison of pyrolysis products for silica-immobilized and liquid bibenzyl.
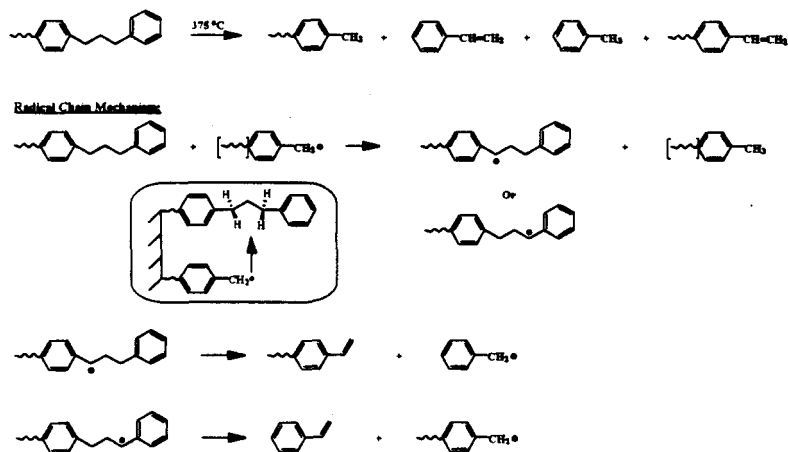

Radical Chain Mechanism

Figure 4. Radical chain propagation steps for the pyrolysis of silica-immobilized 1,3-diphenylpropane. Bracket notation denotes species exists in both gas-phase and surface-attached forms.
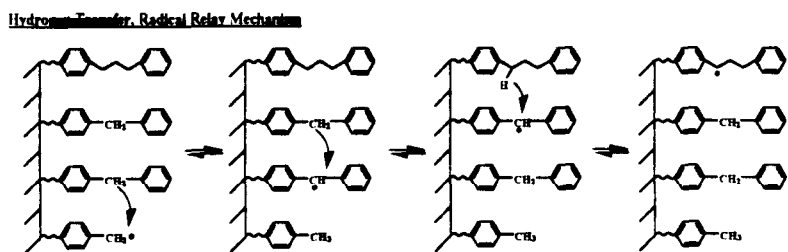
Hydrogen Transfer, Radical Relay Mechanism

Figure 5. Radical relay mechanism in the pyrolysis of silica-attached 1,3-diphenylpropane.