Aromatic Polymers: Synthesis via Nickel Catalyzed Coupling of Aryl Chlorides

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AROMATIC POLYMERS: SYNTHESIS VIA NICKEL CATALYZED COUPLING OF ARYL CHLORIDES

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ABSTRACT

A new method for the formation of high molecular weight aromatic polymers via the nickel coupling of aromatic dichlorides will be described. The novel polymerization is performed in a dry aprotic solvent (e.g., in DMAC) using catalytic amounts of zero-valent nickel, triphenylphosphine or bipyridyl ligands, and excess zinc metal. The reaction must be performed under an inert atmosphere and in the absence of water. In order to obtain high polymer, one must use low amounts of nickel, high triphenylphosphine/nickel ratios, excess zinc metal and moderate temperatures (70°C). Variables such as the choice of ligand or co-ligand, salt addition, ligand and zinc concentrations, allow for optimization of the reaction efficiency. Critical features of the polymerization mechanism will also be reviewed.

The method is general and allows for the preparation of novel monomers and an almost infinite variety of polymers. The two prerequisites for a successful preparation of high molecular weight product are solubility of the monomer, and more particularly of the obtained polymer, in the reaction medium; and the necessity that any functional group(s) present in the monomer(s) (and in the resulting polymer) be inert toward zinc/nickel system. Materials that were prepared via the novel method include polyarylether-

sulfones, polyaryletherketones, polyphenylenes and polyamides. The approach is particularly suited for the synthesis of biphenylene based resins, e.g., polybiphenylene ethersulfone, because coupling of a chlorophenyl moiety creates a biphenyl unit. The latter display a number of highly attractive characteristics, such as high glass transition temperatures, low moisture absorption and extremely high impact strengths and toughness. An intriguing feature of the nickel coupling polymerizations and copolymerizations is encountered in instances that involve aryl chloro dichlorides possessing dissimilar chloro moieties. A number of sequence distributions are then possible in the resulting polymer. In some instances, different microstructures were indeed obtained under different experimental conditions when such "asymmetric" dichlorides were used.

INTRODUCTION

Several methods are available for the preparation of aromatic polymers. Most of them involve the formation of a chemical bond between a carbon atom and a heteroatom. Typical of these are, for example, the aromatic polyarylethersulfones [1-6] and polyaryletherketones [1, 7, 8] which are made via the nucleophilic substitution reaction of an activated aromatic dihalide with phenoxide anions. Carbon-oxygen bonds are formed during the polymerization. Aromatic polycarbo-nates which are prepared by the reaction of a dihydric phenol with phosgene or a derivative thereof are another example [9-11]. A similar situation is encountered with the class of polyarylates - materials from dihydric phenols and aromatic diac-ids [12-14]. Many more examples can be found in the literature.

Polymerizations which involve the formation of an aromatic carbon-carbon bond are not very common. One finds a large number of references which describe efforts to develop such methods. These efforts were unsuccessful. Thus, the oxida-tive polymerization of benzene using a Lewis acid, a cocatalyst and an oxidizing agent was studied extensively by Kovacic and coworkers [15-23]. Low molecular weight polyphenylenes of questionable linearity were obtained. In another effort, polybiphenylenes of very low molecular weight were prepared via the Ullmann reaction of the corresponding diiodo derivatives [24, 25]. Treatment of 4,4'-dibro-mo-2,2'-dimethylbiphenyl with bis(1,5-cyclooctadiene)-nickel(0) [25] also yielded a very low molecular weight material. Oligomeric polyphenylenes were synthesized by the reaction of p-dibromobenzene with magnesium in the presence of transition metal compounds such as $NiCl_2$ -2,2'-bypiridine or $NiBr_2$-(triphenylphosphine)$_2$ [26, 27]. The electroreduction of 4,4'-dibromobiphenyl in the presence of nickel

complexes as catalysts also gave polyphenylene oligomers with an average degree of polymerization of only about 12 [28].

In some instances, however, polymerizations proceeding via the formation of an aromatic carbon to carbon bond were successful. Thus, an elegant oxidative coupling (the Scholl reaction) was described by Percec *et al.* [29]. High molecular weight polymers were obtained by reacting 4,4'-di(1-naphthoxy)diphenylsulfone and 4,4'-di(1-naphthoxy)benzophenone with an equimolar amount of ferric chloride. The drawback of this method is that it requires stoichiometric amounts of the Lewis acid; moreover, it works only with systems capable of undergoing the Scholl reaction, mostly naphthoxy compounds.

The Suzuki reaction [30] which consists of condensing an aromatic boronic acid with a bromoaromatic derivative in the presence of a palladium phosphine complex proceeds in high yields; this makes it attractive for step-growth polymerizations. Polyphenylene type materials were made via this route. Thus, Wegner *et al.* reported the synthesis of alkyl-substituted poly(p-phenylenes) with a number average molecular weight Mn of 21,000 by reaction of benzene bisboronic acids with various dibromo compounds [31]. Water-soluble poly(p-phenylenes) having carboxyl substitution were prepared by coupling boronic acids with aryl halides [32]; the polycondensation was plagued by undesirable side reactions due to the phosphine ligand [33]. The obvious drawback of the Suzuki reaction is the necessity to use boronic acids which render the approach economically prohibitive.

In summary, a method which would allow for the quantitative polycondensation of easily available inexpensive monomers to high molecular weight polymers via aromatic carbon-carbon bond formation is of great practical interest. Work in our laboratories resulted in the development of a facile nickel-catalyzed coupling of aromatic dichlorides to biphenyl derivatives. The reaction proceeds in quantitative yields and under very mild conditions; and it can be applied to the synthesis of a wide number of polymer systems.

DISCUSSION

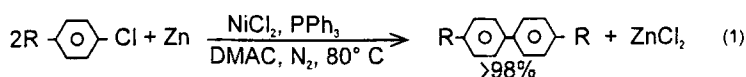The discussion is divided into two parts: Part A describes the reaction, its mechanism and most important variables; as well as the type of polymer which can be prepared via its use. Part B discusses the synthetic work that was performed by our group in the area of polyarylethers; some exploratory experiments with other systems are also shown. Clearly, our work illustrated the broad application potential

of the new method. Selected literature examples that have since been published by others, both in the preparation of polymers and monomers are also provided.

Part A

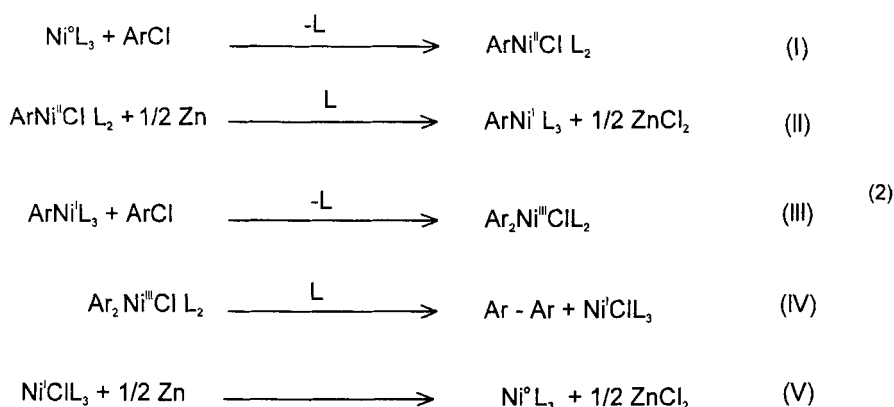*(a) Nickel (o) Coupling of Aryl Chlorides*

The nickel (o) coupling of aryl chlorides was studied in depth in our labor-atories. Conditions under which the corresponding biaryls are obtained in quanti-tative yields were demonstrated [34, 35]. A catalytic amount of nickel-triphenyl-phosphine complex is employed in the presence of excess zinc metal in dry dipolar aprotic solvents at 60-90°C. The reaction is complete within a few minutes. Our process is of particular interest because it allows for the efficient coupling of aryl chlorides. Prior coupling procedures required aryl bromides and iodides.

$$2R \longleftarrow \bigcirc \longrightarrow Cl + Zn \xrightarrow[\text{DMAC, N}_2, 80°\text{C}]{\text{NiCl}_2,\ \text{PPh}_3} R \longleftarrow \bigcirc \longrightarrow \bigcirc \longrightarrow R + ZnCl_2 \qquad (1)$$

Various nickel salts can be employed to generate the catalyst. Nickel chlor-ide and were bromide the most active. Metals such as zinc, magnesium and mang-anese in combination with the nickel catalyst gave high yields of the coupled products from chloroaromatic derivatives. The best ligands were triarylphosphines. Other ligands, e.g. bipyridine, afforded advantages when aryl chlorides possessing electron donating substituents were utilized. In some cases, it was of interest to use a mixture of both ligand types [34, 35]. The addition of salts, for example of sodium chloride, bromide or iodide accelerated the rate of the coupling reaction. This option represents another technique for optimizing the efficiency of the process [34, 35].

Reduction reactions to the corresponding arene take place with materials having acidic substituents such as phenolic hydroxyl or carboxylic acids. Water and other protic sources must be avoided. Aryl chlorides with electron withdrawing or weakly electron donating substituents give high yields of biaryl products. Mono-mers with strong electron-donating substituents, such as methoxyl, produce some reduction products. This side reaction, however, can be suppressed by using 2,2'-bipyridine as the ligand (vide supra).

The following key steps for the nickel coupling reaction of aryl chlorides have been established to fit our experimental data (L represents a ligand , e.g., tri-phenylphosphine):

$$Ni^{\circ}L_3 + ArCl \xrightarrow{-L} ArNi^{II}Cl\,L_2 \qquad (I)$$

$$ArNi^{II}Cl\,L_2 + 1/2\ Zn \xrightarrow{L} ArNi^{I}\,L_3 + 1/2\ ZnCl_2 \qquad (II)$$

$$ArNi^{I}L_3 + ArCl \xrightarrow{-L} Ar_2Ni^{III}ClL_2 \qquad (III)$$

$$(2)$$

$$Ar_2Ni^{III}Cl\,L_2 \xrightarrow{L} Ar - Ar + Ni^{I}ClL_3 \qquad (IV)$$

$$Ni^{I}ClL_3 + 1/2\ Zn \xrightarrow{\hspace{2cm}} Ni^{\circ}L_3 + 1/2\ ZnCl_2 \qquad (V)$$

Step (I), the oxidative addition of ArCl to zero-valent nickel, is very fast and yields a Ni^{II}-terminated species. The latter undergoes reduction [step (II)] which is rate-determining during the early stages of the reaction, when the aryl chloride concentration is high. Towards the end of the reaction, however, step (III) becomes rate determining. Step (IV), which results in the formation of the biaryl, is very fast and yields $Ni^{I}\ ClL_3$; the latter is then reduced [step (V)] to regenerate the Ni°.

In the absence of aryl chloride, the Ni^{I} species of step (II) undergoes a very slow process of biaryl formation as shown:

$$2\ Ar\ Ni^{I}\ L_3 \xrightarrow{-L} Ar_2Ni^{II}\ L_2 + Ni^{\circ}L_3$$

$$\downarrow L \qquad\qquad (3)$$

$$Ar - Ar + Ni^{\circ}L_3$$
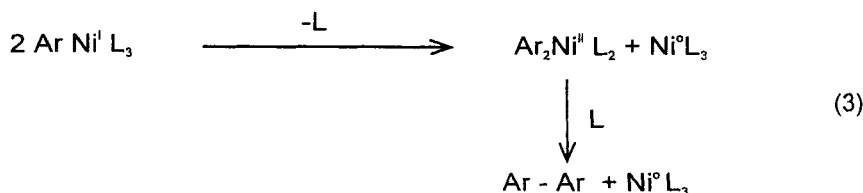
It follows that low levels of nickel are beneficial if rapid formation of high molecular weight polymer is desired.

Electron-withdrawing substituents on the aryl group accelerate both steps (II) and (III). As a result, aryl chlorides with such groups tend to react faster than those with electron-donating substituents. In case mixtures of monomers of different reactivities are used, excessive block formation of the more reactive monomer can be avoided by keeping its relative concentration in inverse proportion to its reactivity.

Aryl groups bearing electron-donating substituents are not only slower reacting; they also promote side reactions that act as polymer terminating steps. The most important of these involves the triphenylphosphine ligand. Triphenyl-phosphine works so well as a ligand in this reaction because it provides a good balance of electron donation to nickel to promote oxidative addition of aryl chloride

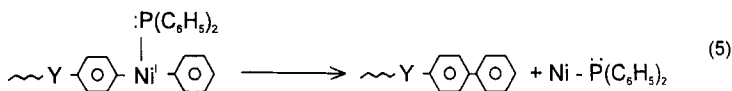and because it is bulky enough to also ensure sufficient amount of coordinative unsaturation of nickel. A delicate balance with respect to the environment in the vicinity of the nickel atom must be maintained. On the one hand, there must be enough coordinative unsaturation to promote oxidative addition of the aryl chloride; on the other hand, if the coordinative unsaturation is too high phenyl transfer from the triphenylphosphine ligand will take place (vide infra). Substituents on the aryl ring play a major role. The equilibrium

$$
Y-\langle \circ \rangle-Ni^{I} \overset{P(C_6H_5)_3}{\underset{P(C_6H_5)_3}{\underset{|}{\overset{|}{\rule{0pt}{0pt}}}}}\!\!\!\!\!\!\!\!-P(C_6H_5)_3 \quad \rightleftharpoons \quad Y-\langle \circ \rangle-Ni^{I}\overset{P(C_6H_5)_3}{\underset{P(C_6H_5)_3}{<}} + P(C_6H_5)_3 \tag{4}
$$
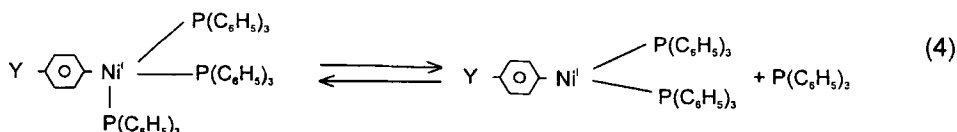
will be shifted to the right when Y is electron-donating because the electronic requirements of the nickel are being met by the aryl substituent rather than by the coordinated triphenylphosphine. This, in turn, increases the coordinative unsaturation of the nickel. At higher levels of coordinative unsaturation the nickel fills its coordination requirements by phenyl transfer from the triphenylphosphine ligand. Our studies have shown that intramolecular transfer of a phenyl group involving ipso substitution of nickel for phophorus takes place. An alternative ortho-metalation mechanism was ruled out by using substituted triarylphosphines.

Reductive elimination from the rearranged species yields a low molecular weight biphenyl-terminated material:

$$
\sim\!Y-\langle \circ \rangle-Ni^{I}\overset{:P(C_6H_5)_2}{\underset{|}{\rule{0pt}{0pt}}}-\langle \circ \rangle \longrightarrow \sim\!Y-\langle \circ \rangle\langle \circ \rangle + Ni-\dot{P}(C_6H_5)_2 \tag{5}
$$

Electron donating groups promote the phenyl transfer reaction by stabilizing the highly coordinatively unsaturated nickel species and by stabilizing the transition state involved in phenyl transfer from phophorus to nickel. The need for relatively high concentrations of triphenylphosphine to produce high molecular weight polymer (see below) is readily explained by this mechanism. The high triphenylphosphine levels are needed to shift the equilibrium of equation (4) to the left; and, accordingly, to minimize the amounts of highly coordinatively unsaturated nickel species which lead to premature termination via phenyl group transfer.

As indicated above, the addition of salts, for example of sodium halides, accelerates the coupling reaction. Figure 1 shows a kinetic plot for the coupling of chlorobenzene at 80°C which is complete in 90 minutes (curve (a)). Examination of this plot reveals that the reaction rate, which is proportional to the slope of the curve,
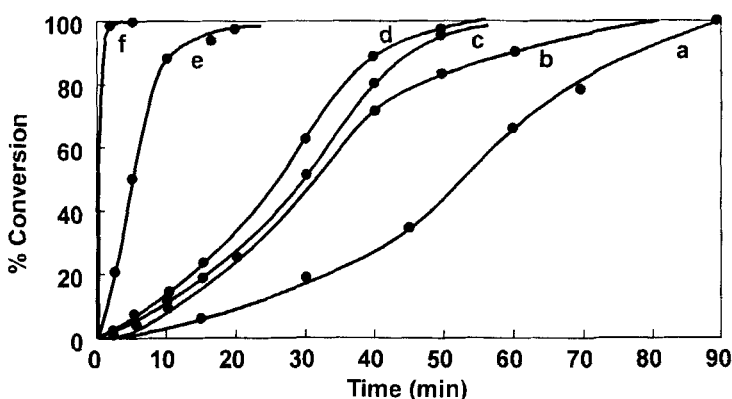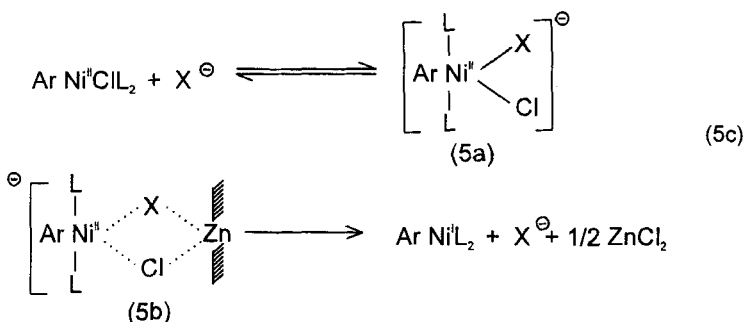
Figure 1. Coupling of Chlorobenzene in DMAC at 80°: A) No Added Salt; B) 1 M NAF; C) 1 M NASO₄; D) 1 M NACL: E) 1 M NABr; F) 1 M N AJ

increases continuously during most of the reaction. This autocatalytic behavior could be due to zinc or chloride ions, since $ZnCl_2$ is a product of the reaction. Experiments with added sodium chloride clearly demonstrate that the autocatalytic behavior is due to the formation of chloride ion. Zinc chloride shows no additional rate enhancement beyond the effect produced by sodium chloride, indicating that metal cationic species play no role in the acceleration.

Figure 1 shows also that all the halides as well as other anions increase the reaction rate; their relative effects are in the order $F < SO_4 < Cl << Br < I$. The effects of bromide and iodide are especially striking. In the presence of sodium iodide the reaction is essentially over in two minutes!

An interesting hypothesis which might explain the role of the anions and the activation parameters observed in their presence, involves the formation of a five-coordinate intermediate in step (II) or (V), Equation (2). The obtained nickelate (5a) could form a bridged Zn complex on the zinc surface, (5b), and thus facilitate the electron transfer, Equations (5c).

$$Ar\ Ni^{II}ClL_2 + X^\ominus \rightleftharpoons \left[Ar\ Ni^{II} \begin{smallmatrix} L \\ | \\ | \\ L \end{smallmatrix} \begin{smallmatrix} X \\ \diagdown \\ Cl \end{smallmatrix} \right]^\ominus \qquad (5c)$$

$$(5a)$$

$$\left[Ar\ Ni^{II} \begin{smallmatrix} L \\ | \\ | \\ L \end{smallmatrix} \begin{smallmatrix} X \\ \cdots \\ Cl \end{smallmatrix} Zn \right]^\ominus \longrightarrow Ar\ Ni^I L_2 + X^\ominus + 1/2\ ZnCl_2$$

$$(5b)$$

(b) Important Reaction Parameters

The important reaction parameters which are required in order to obtain a high molecular weight polymer are listed below.

Solubility

Solubility of the monomer(s) and in particular of the resulting polymer is an absolute requirement if high polymer is desired. The reaction is generally performed in a dipolar aprotic solvent at moderate temperatures of 60-90°C. Precipitation of polymer results in premature termination yielding a low molecular weight material.

Water Removal

This is without question a very important aspect of the entire reaction sequence. It is crucial because in the presence of Ni(o), water reduces aryl halides to the arene; it thus acts as a terminator and it can also deactivate the catalyst [36, 37]. This is the reason why the post reaction azeotrope step has such a large effect on the reduced viscosity (RV) of the polymer produced via the integrated process (vide infra).
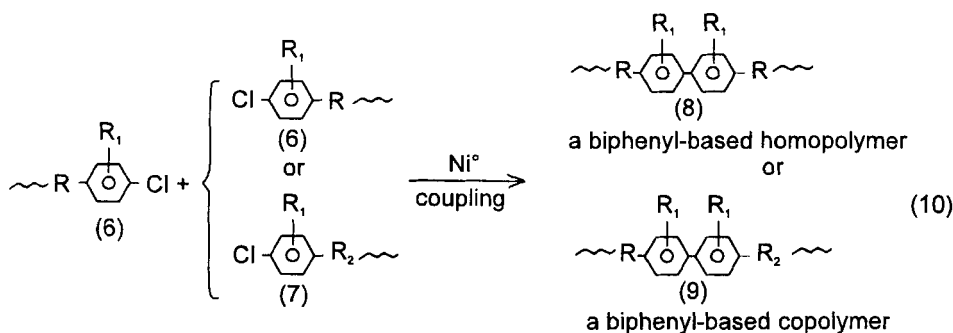
Inert Atmosphere

In the presence of large quantities of triphenyl-phosphine (TPP) small amounts of oxygen can be tolerated. It should be borne in mind, however, that oxygen is a powerful deactivator of the catalyst. The reaction medium is highly reducing in nature; yet it has been found that nickel oxide is not reduced under these conditions. Hence, it is important that an inert atmosphere free of oxygen be main-tained during the reaction.
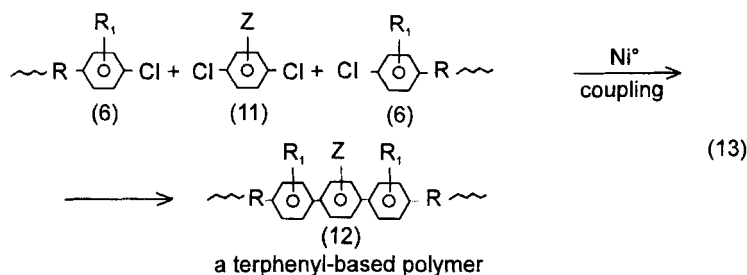
Zinc Purity

This is another important factor for a succesful reaction. The zinc surface must be devoid of zinc oxide and it should have a large surface area. Most failures to produce high polymer can be traced back to poor quality zinc. The catalyst employed in this reaction has the advantage of having a built-in color indicator. The proper color for the reaction mixture is red-brown to brown. Although the reaction mixture will turn greenish on the addition of the monomer, it should begin to display streaks of its characteristic color within a short period of time. A persistent greenish color (especially a deep green) is an indication that nickel halide is not being reduced quickly in the reaction medium, while a grayish color indicates total catalyst deactivation.

(c) Type of Polymer Accessible Via the Nickel Coupling Process

The nickel coupling reaction leads to the formation of an aromatic carbon–carbon bond which in the simplest case results in the formation of a biphenyl moiety. An idealized representation is shown in Equation 10.

$$
\sim\!\! R\!-\!\!\underset{(6)}{\overset{R_1}{\bigcirc}}\!\!-\!Cl \ + \
\begin{cases}
Cl\!-\!\!\underset{(6)}{\overset{R_1}{\bigcirc}}\!\!-\!R\sim \\
\text{or} \\
Cl\!-\!\!\underset{(7)}{\overset{R_1}{\bigcirc}}\!\!-\!R_2\sim
\end{cases}
\xrightarrow[\text{coupling}]{Ni^\circ}
$$

a biphenyl-based homopolymer
or

$$
\sim\!R\!-\!\!\underset{(8)}{\overset{R_1\;R_1}{\bigcirc\!\bigcirc}}\!\!-\!R\sim
$$

$$
\sim\!R\!-\!\!\underset{(9)}{\overset{R_1\;R_1}{\bigcirc\!\bigcirc}}\!\!-\!R_2\sim
$$

a biphenyl-based copolymer   (10)

If R and R_2 are a chemical bond the final product will be a polyphenylene. On the other hand, when R or R_2 are an ether, ester, secondary amide, ketone or any other group which is inert, in the presence of the nickel catalyst, the resulting product will be a condensation polymer incorporating a biphenyl group. Similarly, it is easy to envision how the coupling reaction can lead to terphenyl and higher polyphenyl based resins. This is illustrated below:

$$
\sim\!R\!-\!\!\underset{(6)}{\overset{R_1}{\bigcirc}}\!\!-\!Cl \ + \ Cl\!-\!\!\underset{(11)}{\overset{Z}{\bigcirc}}\!\!-\!Cl \ + \ Cl\!-\!\!\underset{(6)}{\overset{R_1}{\bigcirc}}\!\!-\!R\sim \qquad \xrightarrow[\text{coupling}]{Ni^\circ}
$$

$$
\longrightarrow \ \sim\!R\!-\!\!\underset{(12)}{\overset{R_1\;Z\;R_1}{\bigcirc\!\bigcirc\!\bigcirc}}\!\!-\!R\sim \qquad (13)
$$

a terphenyl-based polymer

Obviously, the reactivities of (6) and (7) (Equation 10), as well as of (6) and (11) (Equation (13) must be about the same in order to obtain structures (9) and (12). If these reactivities differ, block structures will result. As mentioned ear-lier, excessive blockiness can be avoided by keeping the relative concentration of the more reactive monomer in inverse proportion to its reactivity.

In conclusion, the nickel coupling reaction is uniquely suited for the prep-aration of biphenyl, terphenyl and polyphenyl derived materials. Note, that poly-phenyl monomers are expensive and their preparations are often tedious multistep procedures. Inspection of equations (10) and (13), on the other hand, shows that the syntheses of (8), (9) and (12) require comparatively inexpensive raw materials.

Part B

This part is subdivided into sections (I) and (II). Section (I) discusses the pioneering work that was performed by our group. Section (II) provides examples of interest both in the preparation of polymers and monomers that were since published by others.

(I) Synthetic Work

*(a) Polyarylethers Incorporating Biphenyl and/or Terphenyl Moieties*

The preparation of polyarylethers was an area of great interest to our group. Within the family of these materials, in particular of polyarylethersulfones, those that are based on biphenyl and/or terphenyl moieties offer a unique combination of properties. A representative product is polymer (16) which is offered commercially by Amoco Chemicals Polymers Business Group under the trademark RADEL®R-5000. A comparison of basic properties of the materials (14) (UDEL®P-1700 Polysulfone, PSF), (15) (Sumikaexcel®4100 G, Polyethersulfone, PES) and (16) is provided in Table 1.
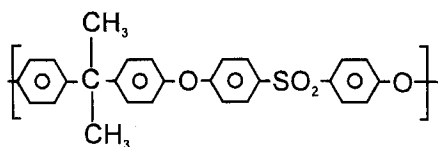
UDEL® P-1700, PSF   (14)
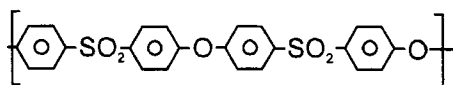
SUMIKAEXCEL® 4100G, PES   (15)
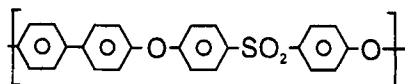
RADEL® R-5000   (16)

The superior performance of polymer (16), a direct consequence of the presence of the biphenyl ring, is readily apparent. The polymer offers a combination of properties which include a high T_g, low flammability, low water absorpion, and most importantly, a very high notched impact strength - the highest of all other engineering polymers in its temperature class. The polymer is also distinguished by improved chemical and environmental stress-crack resistance over other polyaryl-

TABLE 1. Selected Physical and Mechanical Properties of RADEL® R-5000 Polyarylethersulfone, UDEL®P-1700 Polysulfone (PSF), and SUMIKAEXCEL® 4100G Polyethersulfone (PES)

| Property	Test Method	UDEL® P-1700 (14)	SUMIKAEXCEL® 4100G (15)	RADEL® R-5000 (16)
Glass Transition (°C)		190	225	220
Tensile Yield Strength (MPa)	ASTM D-638	70.3	84	69.7
Tensile Modulus (GPa)	ASTM D-638	2.48	2.40	2.34
Elongation at Break (%)	ASTM D-638	75	40	60
Flexural Yield Strength (MPa)	ASTM D-790	106	129	107
Flexural Modulus (Gpa)	ASTM D-790	2.69	2.60	2.41
Notched Izod (J/m)[1]	ASTM D-256	69	83	690
Unnotched Izod[2]	ASTM D-256	NB	NB	NB
Tensile Impact (kJ/m^2)	ASTM D-1822	420	337	400
Heat Deflection Temperature [1.82 MN/m^2][3](°C)	ASTM D-648	174	207	203
Specific Gravity (g/cm^3)		1.24	1.37	1.29
Refractive Index		1.633	1.651	1.672
Water Absorption at Equilibrium (%)	ASTM D-570	0.62	2.1	1.1
Limiting Oxygen Index	ASTM D-286	30	38	38

[1] Measured at a thickness of 3.2 mm.
[2] NB = no break; sample thickness = 3.2mm.
[3] Measured at a thickness of 3.2mm.

ethersulfones (PAES's), and by its retention of ductility and toughness following thermal aging and prolonged hot-wet exposure conditions. In addition, the polyaryl-ethersulfone (16) is uniquely suitable for medical applications; its toughness and transparency are combined with the ability to withstand numerous sterilizations cycles with steam containing morpholine, at pressures of 500 psi and higher.

Other biphenyl and terphenyl derived polyarylethers also display unusual toughness characteristics. Thus, polyarylether (17) which was prepared via the Ullman condensation of bisphenol A with 4,4'-dibromodiphenyl [38] (RV in chloroform = 1.11 dl/g) has a T_g of 175°C, a tensile modulus of 240,000 psi, a tensile strength of 11,000 psi and an elongation of 150%. A similar set of excellent mechanical properties was observed with the terphenyl material (18) which was also made by the Ullman reaction. Both (17) and (18) display notched Izod impact values greater than 500 J/m.
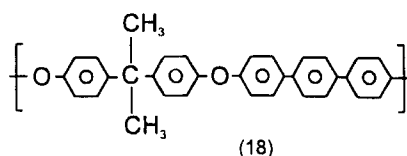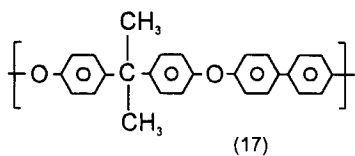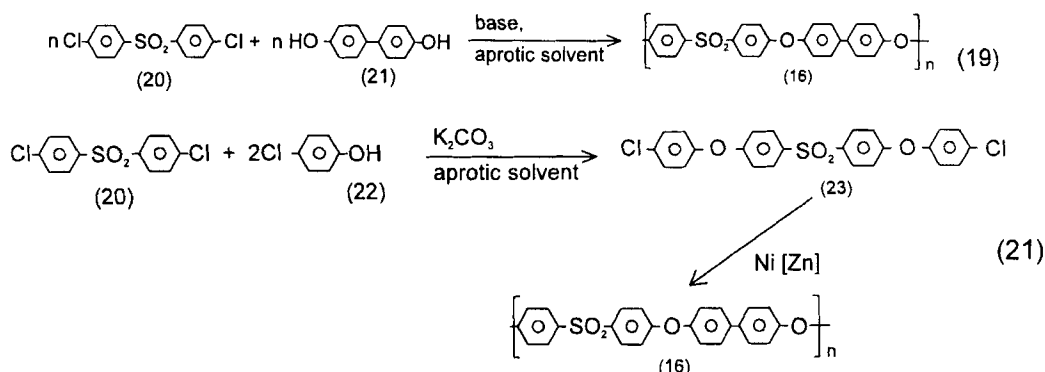

The toughness behavior of these polymers is not fully understood. A dis-cussion of the possible factors was presented in a recent publication [39].

A useful characteristic of polyarylethersulfones based on biphenyl contain-ing repeat units is their improved ability to form alloys. These resins were found to be miscible with selected polyimides and poly(amide-imides) [40]. Moreover, good mechanical compatibility was observed upon alloying these polyarylethersulfones with other polyarylethersulfones, as well as with polyaryletherketones, although the blends had limited solubility [41].

(b) Synthesis of Polymer (16) (RADEL®R-5000) Via the Nickel Coupling Route

Polymer (16) is made commercially via the nucleophilic aromatic substi-tution shown in Equation 19. An approach involving the nickel coupling method which would obviate the necessity of using the relatively expensive 4,4'-biphenol monomer, was therefore investigated, (Equation 21). It comprised two steps: the preparation of the intermediate dichloro derivative (23) which would then be self-polymerized to polymer (16). The first step, i.e. the condensation of p-chlorophenol with 4,4'-dichlorodiphenylsulfone is a classical nucleophilic aromatic substitution and yielded the dichloro product in quantitative yield. However, a detailed study to determine the optimum conditions for its self-condensation in the presence of the nickel(o) catalyst had to be performed.

$$n\ Cl\!-\!\langle o \rangle\!-\!SO_2\!-\!\langle o \rangle\!-\!Cl\ +\ n\ HO\!-\!\langle o \rangle\!-\!\langle o \rangle\!-\!OH \xrightarrow[\text{aprotic solvent}]{\text{base,}} \left[\langle o \rangle\!-\!SO_2\!-\!\langle o \rangle\!-\!O\!-\!\langle o \rangle\!-\!\langle o \rangle\!-\!O\right]_n \quad (19)$$

(20)   (21)   (16)

$$Cl\!-\!\langle o \rangle\!-\!SO_2\!-\!\langle o \rangle\!-\!Cl\ +\ 2 Cl\!-\!\langle o \rangle\!-\!OH \xrightarrow[\text{aprotic solvent}]{K_2CO_3} Cl\!-\!\langle o \rangle\!-\!O\!-\!\langle o \rangle\!-\!SO_2\!-\!\langle o \rangle\!-\!O\!-\!\langle o \rangle\!-\!Cl$$

(20)   (22)   (23)

$$\xLeftarrow{Ni\ [Zn]} \qquad (21)$$

$$\left[\langle o \rangle\!-\!SO_2\!-\!\langle o \rangle\!-\!O\!-\!\langle o \rangle\!-\!\langle o \rangle\!-\!O\right]_n$$

(16)

Initial attempts to polymerize monomer (23) proved disappointing in spite of the fact that it, as well as the N,N-dimethylacetamide solvent, were carefully purified and dried; also, the use of very low amounts of catalyst as predicted by our mechanistic studies (vide supra) did not lead to high moloecular weight polymer. It was, therefore, decided to use statistical experimental design. Thus, a sixteen experiment, two level fractional factorial design was used to study the effect of nine variables on polymer molecular weight. The variables examined were: the amount of nickel chloride, the amount of excess zinc, the amount of solvent, the reaction temperature, the amount of triphenylphosphine (TPP), the amount of bipyridine, the reaction time, the methods used to dry the solvent, and length of time between active catalyst (Ni(o)) generation and reaction with monomer. Three variables had a truly significant effect (> 95% confidence level) on the molecular weight, as measured by the reduced viscosity (RV) of the polymer. The most significant variable was the amount of triphenylphosphine (estimated effect = 0.232 on the reduced viscosity of the polymer in going from low to high TPP levels). Interestingly, studies with aryl chloride couplings had not shown a great dependence on the amount of triphenylphosphine. A possible explanation of this discrepancy may be the fact that a yield of 95% is considered excellent in monomer chemistry; on the other hand yields of the order of 99% and higher are required to make high polymer. The next important variable was the reaction temperature whose effect was negative. This was consistent with previous studies which showed that an increase in reaction temperature caused an increase in undesirable side reactions. As predicted, there was a negative effect due to the level of nickel. Less statistically significant was a real positive effect due to the amount of zinc. The data are summarized in Table 2. Using this information it was a simple task to define conditions under which high molecular weight RADEL®R-5000 (RV's > 0.5 dL/g) could be prepared. Comparison of its properties to those of polymers made via the nucleophilic substitution

TABLE 2. Significant Variables in Nickel Coupling to Produce Polyarylethersulfones as Determined by Experimental Design

Variable	Effect on RV	Confidence Level(1)
NiCl$_2$	-0.084	>95%
Zn	0.061	>90%
Reaction Temperature	-0.103	>99%
TPP	0.232	about 100%

(1) Based on the precision of replicated runs.

TABLE 3. Properties of Polyarylethersulfone (16) Produced by Conventional Process and Nickel Coupling

Property	Conventional	Nickel Coupling
Reduced Viscosity (dl/g)	0.57	0.81
T$_g$ (°C)	215	215
1% Secant Modulus (psi)(1)	217,000	238,000
Tensile Strength (psi)	9,730	9,650
Yield Elongation (%)	7.0	7.0

(1) Moduli were determined using crosshead travel to determine strain.

is given in Table 3. As can be seen, the properies are practically identical. The two materials also had comparable toughness. Note that the values quoted in Table 3 were obtained on compression molded samples and should not be compared to those of Table 1 which were generated from injection molded specimens.

Having successfully prepared high molecular weight polymer (16) via the nickel coupling route, we turned our attention to the possibility of performing the two steps of Equation 21 in an integrated manner, i.e., without isolating and purifying the dichloro intermediate (23) [4,4'-di(p-chlorophenoxy) diphenyl-sulfone]. Monomer (23) was synthesized by the reaction of two moles of p-chlorophenol with one mole of 4,4'-dichlorodiphenylsulfone in N,N-dimethyl-acetamide/toluene with potassium carbonate as the base. Upon completion of the reaction, the mixture was coagulated in methanol/water and the precipitate was then recrystallized thrice from isopropanol, followed by drying in a vacuum oven prior to polymerization. In principle, an integrated process involving monomer formation with azeotropic removal of the water of reaction, filtration to remove the potassium

salts (excess potassium carbonate and KCl), and reaction with Zn and Ni(o) to form polymer, appeared possible. The economic advantage of such a process is obvious.

Pertinent experimentation has quickly determined that the most important factor for obtaining high molecular weight polymer was the removal of water formed during the preparation of the intermediate (23). Keeping this important variable in mind, it was possible to prepare materials, without isolation of the intermediate dichlorodiphenoxy derivative, having reduced viscosities as high as 1.17 dL/g.

In an additional effort to determine the breadth of the scope of the nickel-catalyzed polymerizations, monomers were prepared as in Equation 21, except that the mole ratio of p-chlorophenol to 4,4'-dichlorodiphenylsulfone was less than 2. The monomer obtained when this ratio is 1:1 is of particular interest, (Equation 26).
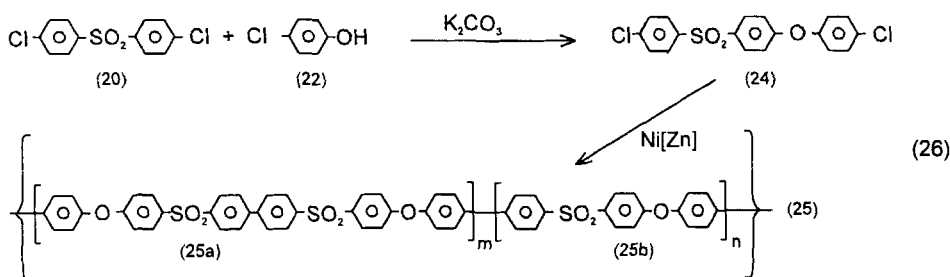
The reaction yields monomer (24) which has two chlorine atoms whose reactivities in the nickel coupling reaction are considerably different. Hence, the obtained polymer (25) will comprise both structures (25a) and (25b). Kinetic experiments were performed to asses the relative differences in reaction rates of the aryl chlorides employed. The relative rate differences were inferred by following the disappearance of monomers in reaction systems. Using this method, the following relative rate data are estimated under the general nickel/zinc aryl chloride coupling procedure.

TABLE 4 Properties of Polymers Obtained by Varying the PCP:DCDPS Ratio in the Monomer Reaction

$$Cl-\langle\bigcirc\rangle-SO_2-\langle\bigcirc\rangle-Cl + X\ HO-\langle\bigcirc\rangle-Cl \xrightarrow{\quad K_2CO_3 \quad}$$

Property	X=2	X=1	Polymer X=1.5	Control(1)
Reduced Viscosity (dl/g)	0.81	0.69	0.60	0.78
T_g (°C)	215	265	235	265
1% Secant Modulus (psi) (2)	238,000	229,000	248,000	240,000
Tensile Strength (psi)	9,650	10,800	11,000	10,500
Yield Elongation (%)	7.0	8.0	7.7	8.0
Pendulum Impact (ft-lbs/in³)(3)	166	176	126	150

(1) Polymer made via the nucleophilic route, equation (31).
(2) Moduli were determined using crosshead travel to determine strain.
(3) The pendulum impact was measured on 0.02" compression molded strips; it is an internally developed test analogous to the Charpy impact test for measuring unnotched toughness.

Units (25a) of copolymer (25) result from the coupling of the very reactive p-sulfonylphenyl chloride (29); repeat units (25b), on the other hand, are formed from the least reactive phenoxyphenyl chloride (27). Based on the relative rate data, a kinetically controlled polymerization reaction should yield copolymer (25) wherein, the ratio of repeat units (25a)/(25b) is about 10. This means that the copolymer (25) should possess properties that are about the same as those of the homopolymer (25a). We were able to demonstrate that such is indeed the case. Thus, homopolymer (25a) can be prepared via the nucleophilic route as shown in equation (31). The data of Table 4 show the properties of both products, i.e., (25) made via the nickel coupling route (equation (26)); and (25a) made via the nucleophilic method (Equation 31). The resins are practically identical.

$$n\ Cl\langle\circ\rangle SO_2 \langle\circ\rangle\langle\circ\rangle SO_2 \langle\circ\rangle Cl + n\ HO\langle\circ\rangle\langle\circ\rangle OH \xrightarrow[\text{aprotic solvent}]{\text{base,}}$$

(30)   (21)

$$\xrightarrow{\hspace{2cm}} \left[\langle\circ\rangle O\langle\circ\rangle SO_2 \langle\circ\rangle\langle\circ\rangle SO_2 \langle\circ\rangle O\langle\circ\rangle\right]_n$$

(31)

(25a)
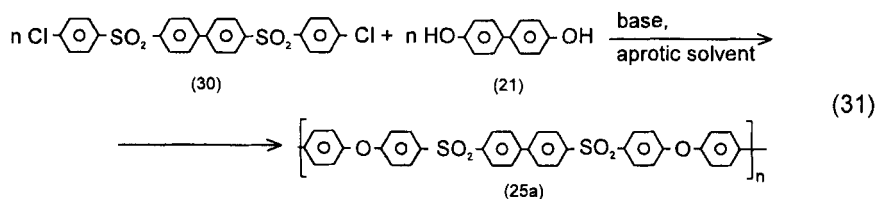
Another interesting aspect of these reactions is that by varying the ratio of p-chlorophenol (PCP) to 4,4'-dichlorodiphenylsulfone (DCDPS) in the synthesis of the monomer, one is able to vary the T_g's of the polymers resulting from the nickel coupling process within a wide temperature range. Thus, the glass transition temperature of material (25) is 265°C; the material derives from the monomer obtained when the ratio of PCP to DCDPS is 1:1. On the other hand, the T_g of product (16) [PCP/DCDPS=2/1, see Table 3] is 215°C. It follows that by varying the ratio of PCP to DCDPS from 2:1 to 1:1 (or even lower), one can obtain polyarylethersulfones whose glass transition temperatures will vary from 215 to 265°C or even greater. Such is the case as illustrated by the data of Table 4. The dichloro intermediates resulting from the condensation of p-chlorophenol with DCDPS at ratios that were between 2 and 1 were oily products. Their isolation and purification would have presented serious problems had it not been for the possibility of performing the reactions via the integrated process (see above). Note, that the data of Table 4 were obtained on compression molded films.
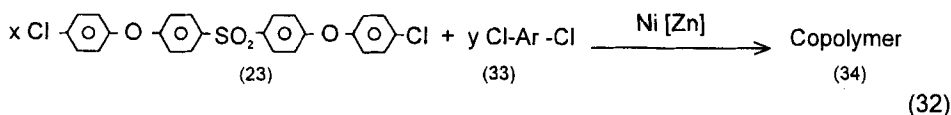
(c) Copolymerizations

Further studies have shown that the nickel coupling reaction is very general and allows for the preparation of an almost infinite number of polymers. This was initially demonstrated by copolymerizing the dichloro diphenoxy derivative (23)

TABLE 5. Properties of High Polymers Produced by the Copolymerization of 4,4'-bis(p-chlorophenoxy) diphenysulfone (23) and Aryl Dichlorides
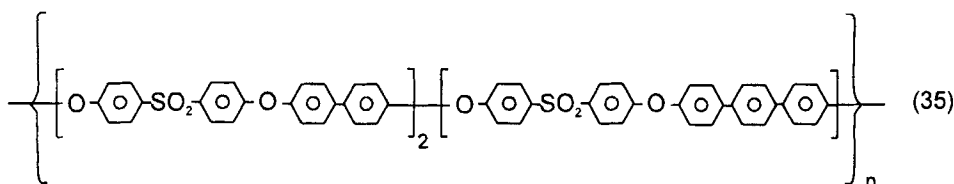
No	Aryl Dichloride	Wt. %	RV (dl/g)	Tg (°C)	1% Secant Modulus (psi)	Tensile Strength (psi)	Pendulum Impact (ft-lbs/in^3)
1	None	-	0.81	215	238,000	9,650	166
2	4,4'-Dichlorodiphenylsulfone	15	0.69	225	232,000	9,870	138
3	4,4'-Dichlorodiphenylsulfone	20	0.55	230	255,000	10,200	120
4	p-Dichlorobenzene	10	0.56	218	234,000	9,840	179
5	4,4'-Dichlorobenzophenone	10	0.58	210	227,000	9,620	147
6	Ethylene Bis(p-chlorobenzoate)	10	0.54	200	243,000	10,300	147
7	2,5-Dichlorothiophene	10	0.40	-	-	-	-

with a series of comonomers, (Equation 32). A number of high polymers were obtained. They are listed in Table 5, all data being generated on compression molded samples.

$$x \; Cl \; \text{—⟨o⟩—} \; O \; \text{—⟨o⟩—} SO_2 \text{—⟨o⟩—} O \text{—⟨o⟩—} Cl \; + \; y \; Cl\text{-Ar -Cl} \; \xrightarrow{\text{Ni [Zn]}} \; \text{Copolymer}$$

(23)   (33)   (34)

(32)

Note that the 1% secant moduli cited in Table 5 were determined using crosshead travel to determine strain; the definition of the pendulum impact is given in footnote [3], Table 4.

The structures of some of the copolymers listed in Table 5 are of interest. For example, the copolymerizations involving p-dichlorobenzene should yield materials possessing terphenylene units. Moreover, due to the high reactivity of p-dichlorobenzene in the Ni(o)/Zn system (electron withdrawing substituent on the aryl halide, vide supra) the probability that higher polyphenylene groups are formed is very strong. The 10 wt% (26.3 mole%) copolymer of (23) with p-dichloro-benzene (Table 5, item No. 4) is a high molecular weight soluble resin. The use of 15 wt% (36.2 mole%) of p-dichlorobenzene results in a product that is partially soluble in NMP. Premature precipitation takes place at 20 wt% (44 mole%) levels or higher of p-dichlorobenzene. All of the experiments were performed by simultaneously charging all of the monomers into the reaction mixture.

$$\left\{ \left[O \text{—⟨o⟩—} SO_2 \text{—⟨o⟩—} O \text{—⟨o⟩—⟨o⟩} \right]_2 \left[O \text{—⟨o⟩—} SO_2 \text{—⟨o⟩—} O \text{—⟨o⟩—⟨o⟩—⟨o⟩} \right] \right\}_n \quad (35)$$

In the case of the 10 wt% (26.3 mole%) p-dichlorobenzene copolymer we should have approximately one terphenyl-containing repeat unit for every two biphenyl-containing units. The idealized structure of this soluble material is (35), although units with higher polyphenyls will also be present.

As the amount of p-dichlorobenzene is increased to 15 wt% (36.2 mole%), coupling to form 4,4'-dichlorobiphenyl will become of increasing importance. Incorporation of the latter into the copolymer will yield quaterphenyl-containing structures (37). Structures having a sequence of five and six rings will also be formed; and their amount will increase at the 20 wt% p-dichlorobenzene level. Moreover, because of the considerably higher reactivity of p-dichlorobenzene

relative to that of the dichlorodiphenoxy monomer (23), the polyphenyl-containing units (e.g. (37)) will tend to form in the initial stages of the reaction yielding crystalline insoluble block structures. A staged feed of p-dichlorobenzene to the reaction mixture should overcome the above block-forming course of the polymerization. A staged feed should also result in a decreased amount of the crystalline higher polyphenyl-containing repeat units.
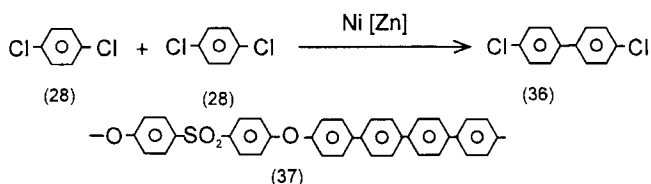
The product obtained from the dichlorodiphenoxy monomer (23) and 4,4'-dichlorodiphenylsulfone (Table 5, items 2 and 3) is another interesting case. The sulfone starting material is very reactive (vide supra). Hence, formation of units (38), flanked on both sides by an SO_2 group, is expected to predominate during the initial stages of the reaction. As the polymerization proceeds, units (39) and finally (40) will also form.

The reaction, therefore, leads to a product which incorporates three types of biphenyl units. Comparison of the glass transition temperatures of polymers 1, 2, and 3 (Table 5) shows that the T_g's increase as the amount of the 4,4'-dichloro-diphenylsulfone comonomer increases. This is due to units (38) and (39); higher weight proportions of structures $ArSO_2$-versus ArO- lead to materials with higher T_g's.
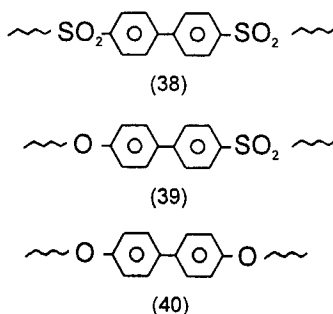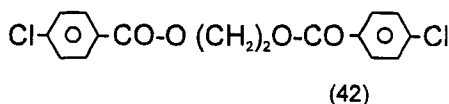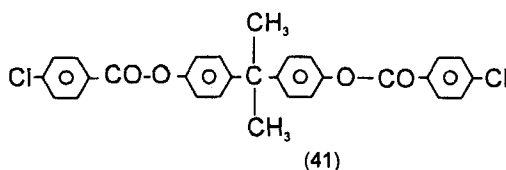

It is interesting to note that high polymer was formed at both the 15 and the 20 wt% level of sulfone. It is anticipated that even higher wt. percentages of sulfone would lead to soluble products. This is due to the fact that polydiphenylsulfone displays better solubility than polyparaphenylene. Hence, under our experimental con-

ditions (simultaneous addition of all reagents to the reaction mixture) the more crystalline (i.e. less soluble) the homopolymer, the less of the corresponding monomer can be tolerated in order to obtain a high molecular weight copolymer. It should be noted that experiments with a staged feed of 4,4'-dichlorodiphenylsulfone are certainly worthwhile. Under staged conditions soluble copolymers having a different sequence distribution of the diphenylsulfone units are expected to be formed. The experimentation should provide very important insights on the effect of sequence distribution on a number of polymer properties. The area is definitely worthy of additional study because unique polymer structures are accessible via the above terpolymerizations.

(d) Exploratory Scanning Experiments

A series of exploratory scanning experiments was performed in our laboratories to demonstrate the broad applicability of the new nickel coupling process. No optimization studies were attempted with any of the monomers used.

$$\text{Cl-}\bigcirc\text{-CO-O-}\bigcirc\text{-}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{-}\bigcirc\text{-O-CO-}\bigcirc\text{-Cl}$$

(41)

$$\text{Cl-}\bigcirc\text{-CO-O (CH}_2)_2\text{O-CO-}\bigcirc\text{-Cl}$$

(42)

Coupling of the dichloro ester (41) led to a polyester having an RV of 0.18 dL/g. Another polyester (RV= 0.10 dL/g) was made from the starting diester (42). It was thus demonstrated that biphenyl based polyesters could be prepared via the new polymerization.

A polymer with an RV of 0.18 dL/g was also made by the self polymerization of 4,4'-dichlorodiphenylsulfone. On the other hand, insoluble powders resulted when coupling was attempted with monomers such as 4,4'-dichloro-benzophenone or 2,5-dichlorothiophene.

The findings confirmed that as long as the monomer and, more importantly the polymer, are soluble in the aprotic solvent at the moderate temperatures employed for the coupling (60-90°C); and as long as the monomer does not carry a group susceptible to reaction with the nickel catalyst, a very large number of polymeric structures are accessible via the Ni(o)/Zn process. Our research has also

demonstrated the possibility of using inexpensive monomers such as p-dichloro-benzene to synthesize unique products with very interesting properties.

(II) Synthetic Work Performed in Other Laboratories

(a) Polymers

While the polymerization of 4,4'-dichlorobenzophenone (vide supra) yielded an insoluble powder, the self-condensation of the corresponding imine derivative (43) led to polymer (44) having an inherent viscosity of 0.36 dL/g (NMP, 30°C), (Equation 45) [42, 43]. It appears that limited solubility of (44) was the reason that higher molecular weight material was not obtained. The amorphous polymer (44) had a T_g of 225°C and displayed very good temperature resistance (5 wt% loss in nitrogen at 558°C). Hydrolysis in 10% HCl gave the completely insoluble poly(4,4'-benzophenone) (46) which was also very thermally stable (5 wt% loss temperatures of 510 and 560°C in air and nitrogen, respectively).
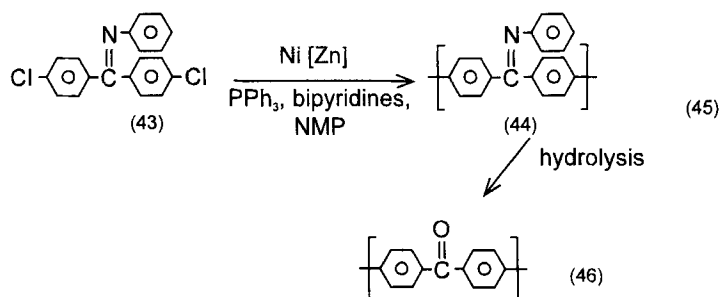

The polymerization of 2,5-dichlorobenzophenone (47) was studied by two groups [42, 43 and 44], (Equation 49). High molecular weight (inherent viscosities of 0.87-1.6 dL/g) benzoyl-substituted polyparaphenylenes (48) were obtained.
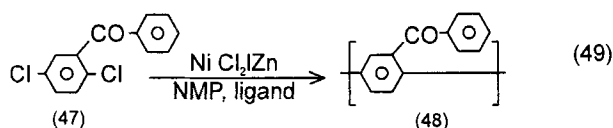

It is remarkable that the ligand had a profound effect on the polymer microstructure [44]. Triphenylphosphine as ligand yielded material (48a). It was found that the reaction was considerably accelerated in the presence of sodium iodide. Thus, (48a) with an inherent viscosity of 1.39 dL/g was obtained after 60 hours at 70°C; in the presence of 1 mole equivalent of sodium iodide (relative to Ni) the polymerization yielded the same polymer having a (η_{inh} of 1.6 dL/g after only 10 hours at the same temperature. Product (48b) resulted when the ligand was a

mixture of triphenylphosphine/2,2'-bypiridine [44]. Polymer (48a) was soluble in chloroform, sym-tetrachloroethane and in mixed solvents 5-15% of phenol in methylene chloride. Polymer (48b), on the other hand, was soluble in the same solvents and also in THF in which (48a) was not. Moreover, the glass transitions of the two resins were markedly different. At comparable molecular weights (inherent viscosities of 1.1 and 0.99 dL/g) the T_g's were 149°C for (48a) versus 217°C for (48b). Based on spectral evidence it was proposed that the differences between (48a) and (48b) are due to different regiochemical placements of the benzoyl group along the polymer chain. Specifically, (48b) was thought to have more of the triad repeat units in the regular H-T, H-T (head-to-tail) arrangement; while a more random distribution of the four possible triads was thought to exist in polymer (48a). Possible mechanistic reasons why such differences in the microstructure were caused by the addition of 2,2'-bipyridine to triphenylphosphine were discussed [44].

The polymers appeared to be amorphous and had good thermal and mechanical properties. Less than 3 wt% loss was noted upon heating in air or in nitrogen to 500°C; tensile strengths at break and tensile moduli were about 0.9 GPa and > 6GPa, respectively.
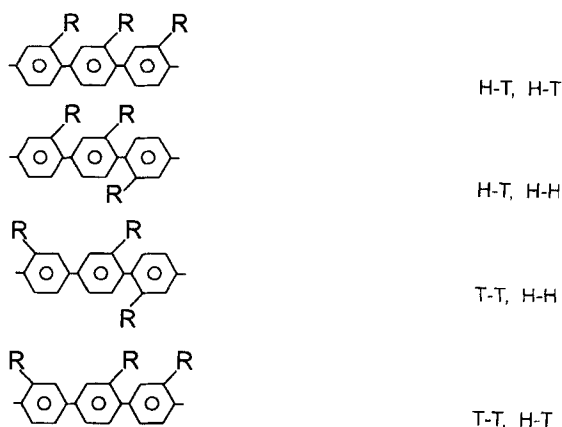
Polymerization of the dichloro compound (50) yielded the amorphous polyketone (51) [45], (Equation 52). The reaction was complete after 2.5 hours. Polymer (51) had an inherent viscosity of 0.52 dL/g (0.5 g /100 ml. of chloroform at 25°C). Its molecular weights were: Mn = 21,000 and Mw = 46,500 as measured by GPC using polystyrenes as standard. The material (51) was cyclized to the polyisoquinoline (53) and the polyphthalazine (54); the latter were cast to tough, flexible and creasable films. Interestingly, a brittle film was obtained upon casting of (51).
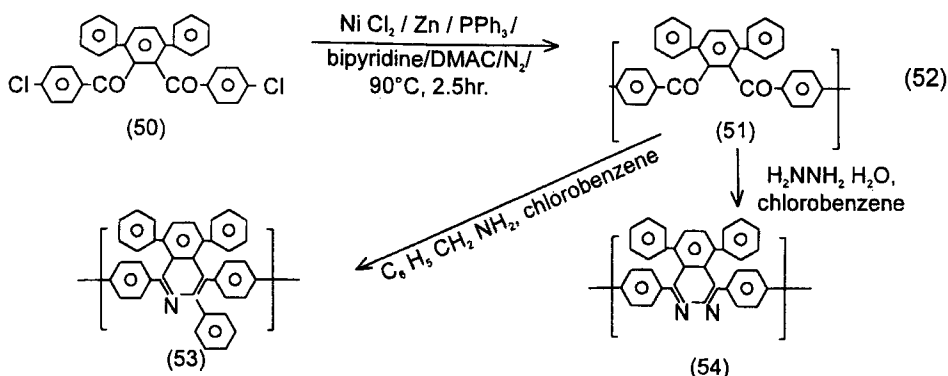
The nickel coupling reaction was used widely to prepare polyphenylenes [46, 47, 48]. For example, two patents to Bayer [46, 47] describe the polymerization of a number of p-dichlorobenzene compounds. Alkoxycarbonyl substitution gave products of high molecular weight, e.g. (55). Dichloro derivatives such as 4,4'-dichlorodiphenyl ether or 4,4'-dichlorobenzophenone, led, as expected, to low polymers. Polyparaphenylene (56) was obtained from p-dichlorobenzene. Its degree of polymerization, based on elementary analysis and assuming that both ends of the polymer chain are chlorine atoms, was 16.
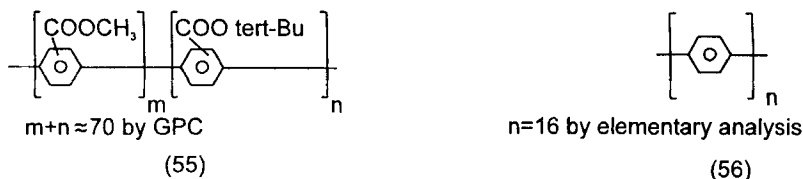

Ueda et al. [49] prepared poly-tert-butoxycarbonyl-p-phenylene having Mw of 20,000 and Mn of 10,000 (GPC), by the polymerization of the corresponding dichloro material. The hydrolysis and decarboxylation of the polymer to polyparaphenylene were studied.

The polymerization of substituted m-dichlorobenzenes is described in reference [50]. Products with inherent viscosities of up to 0.56 dL/g were obtained. The same group (Ueda et al.) investigated also the Ni/Zn mediated polycondensation of 3-phenyl-2,5-dichlorothiophene as well as that of other thiophene derivatives [51,52].

The synthesis of poly-p-terphenylenes having the structure (57) was studied [53]. The solubility of the products increased with the bulkiness of the substituents, but was insufficient for the determination of their molecular weights. Degrees of polymerization were derived from the measurements of their halogen contents. Values of n between 20 and 80 were obtained. However, the inherent viscosities

were low (0.10-0.15 dL/g). The conductivity, after doping with iodine or ferric chloride, was also investigated and the results were comparable to those of poly-p-phenylene.

$$\left[\underset{R_1}{\overset{}{\diagdown}} \right]_n \quad (57)$$
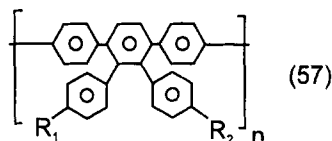
The nickel coupling polycondensation was also applied to the preparation of polyaryletherketones [54, 55]. The main problem in obtaining high molecular weight polymer was the insolubility of the crystalline PAEK's. Relatively high viscosities were achieved, however, when the solubility of the polymer was improved. This is illustrated in the case of the four polyaryletherketone precursors shown in formula (58). The polymerization of monomers 1a and 1c resulted in the precipitation of very low molecular weight crystalline products. The reaction of monomer 1b proceeded homogeneously with a changeover to a heterogeneous system. Monomer 1d, on the other hand, yielded a homogeneous reaction mixture. Optimization studies with 1d allowed for the preparation of a polyaryletherketone with an inherent viscosity of 0.87 dL/g (at 0.5g/100 ml., NMP, at 30°C).
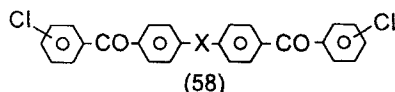
la: X= -O- ; both chlorines in para position

lb: X= -O- ; both chlorines in meta position

lc: X= -O-⟨O⟩-O- ; both chlorines in para position

ld: X= -O-⟨O⟩-O- ; both chlorines in meta position

(58)

The synthesis of biphenyl-based polyamides via the Ni/Zn polymerization is discussed in Reference [56]. Experiments with model compounds have shown that coupling of aromatic chlorides containing primary amide groups does not yield the corresponding diphenyl derivatives; instead reduction products of the starting chloro compounds are obtained. On the other hand, the reaction proceeded smoothly and in high yield with secondary amides. The polymerization of a series of piperazine based dichlorodiamides was studied. Once again, the most critical factor was the polymer solubility. Polymers with inherent viscosities of up to 0.38 dL/g (0.5 g/100 ml. of conc. sulfuric acid at 30°C were prepared.
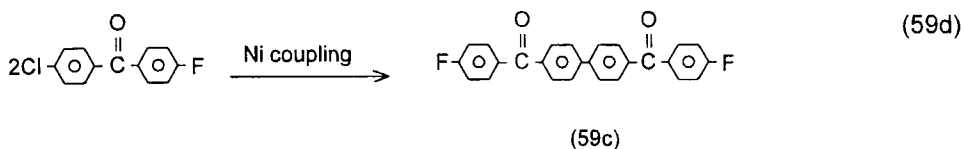
(b) Monomers

The nickel coupling process is very useful for the synthesis of biphenyl-containing monomers. The latter are very often difficult to prepare by other routes

which may require tedious multi-step reaction sequences. Two examples are shown in Equations 59 [57].

(59a), >99%

(59)

(59b), 88%
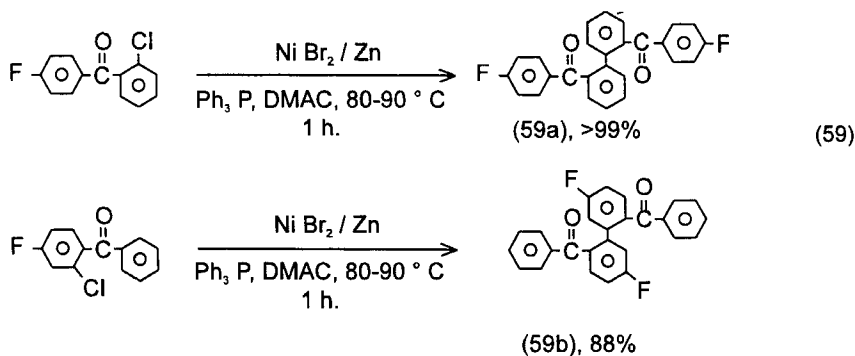
Both (59a) and (59b) were used for the synthesis of polyaryletherketones [57].

A commercial application of nickel coupling was the synthesis of the 4,4'-bis (4-fluorobenzoyl)biphenyl monomer (59c) as shown in Equation 59d [58].

(59d)

(59c)

Interesting examples of the preparation of cyclic monomers and their polymerization to high molecular weight polyaryletherketones were described by researchers at ICI, Ltd. [59,60]. Thus, Compound 60a, (Equation 60), was reacted under Friedel-Crafts conditions with para-chlorobenzoyl chloride to yield the dichloro-terminated material (60b). The latter was treated with Ni/Zn/triphenylphosphine to give the cyclic oligomer (60c). This reaction was performed under pseudo-high dilution conditions [61, 62]. Two other cyclic oligomers (61) and (62) were made in a similar manner. All three cyclic oligomers underwent smooth nucleophilically initiated ring opening polymerization as illustrated in Equation 63.

CONCLUSIONS

The nickel coupling reaction and its application to the synthesis of a variety of biphenylene polymers and monomers is described. Aromatic biphenylene polymers display a number of highly attractive features which are discussed. Biphen-

(60)

(61) (62)

(63)
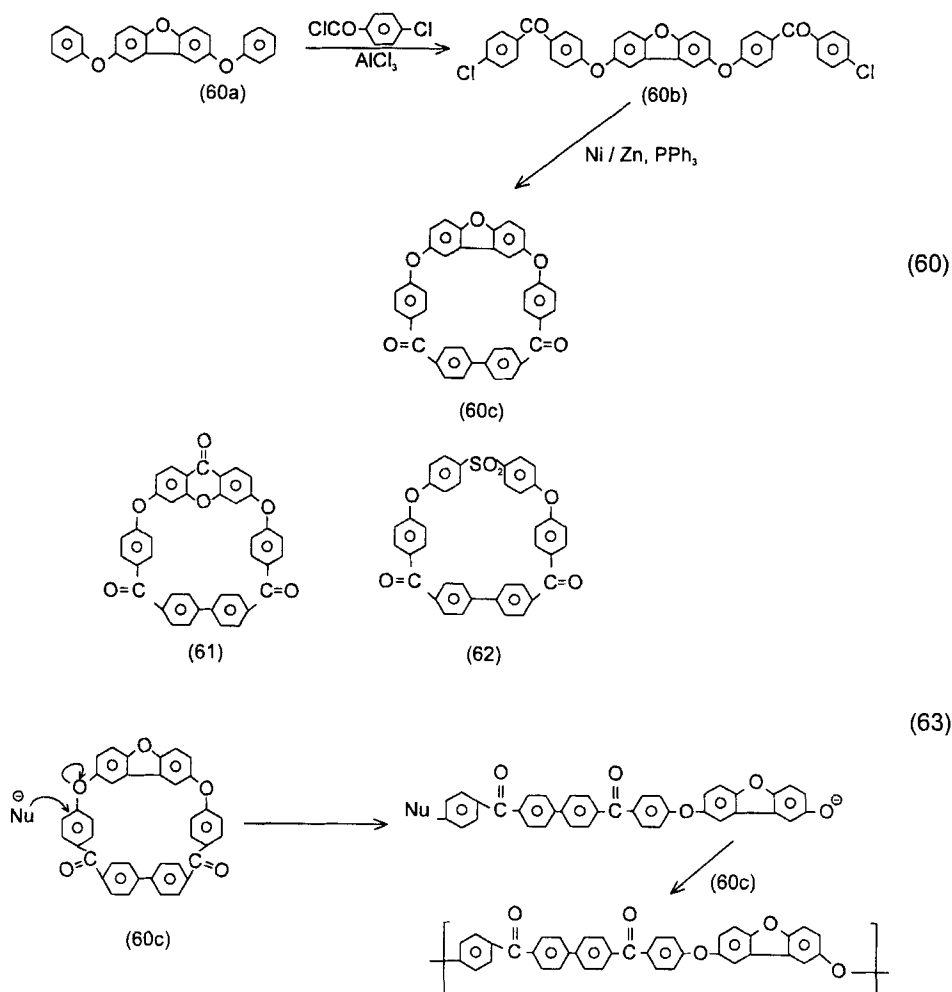
ylene monomers, on the other hand, often require tedious multistep preparative procedures. The novel reaction is performed in a dry aprotic solvent (e.g. DMAC or NMP) using catalytic amounts of zero-valent nickel, a ligand (e.g. triphenylphos-phine or 2,2'-bipyridine) and excess zinc metal. The reactions must be performed under an inert atmosphere and in the absence of water. In order to obtain high polymer one must use low amounts of nickel, high triphenylphosphine/nickel ratios, excess zinc metal and moderate temperatures (60 to about 90°C). Variables such as the choice of ligand or coligand, salt addition, ligand and zinc concentration, etc. allow for optimization of the reaction efficiency. Critical features of the reaction mechanism are reviewed.

The method is general and allows for the preparation of an almost infinite number of aryl monomers and polymers. The prerequisites for a succesful polym-

erization are the solubility of the monomer(s), and more particularly of the obtained polymer in the reaction medium; and the necessity that any functional groups present in the monomer(s) and in the resulting polymer be inert towards the nickel/zinc system. Polymers prepared via the nickel coupling route include poly-arylethersulfones, polyarylketones, polyaryletherketones, polyesters, polyamides, polyphenylenes, polyterphenylenes and polythiophenes. Note, that different micro-structures are possible with aryl dichlorides having dissimilar chloro moieties, and this aspect of the Ni(o)/Zn polycondensations is an additional feature of considerable interest. Finally, biphenylene based monomers (both linear and cyclic) that are valuable starting materials for the synthesis of new resins, were also made via the nickel route.

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