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Summary and Conclusions
7.1 Summary and Conclusions

The progressive dwindling of fossil resources coupled with the increase in oil prices has sparked an intense activity in search for alternatives based on renewable resources for the production of energy. Given the predominance of petroleum- and carbon-based chemistry for the manufacture of organic chemical commodities, a similar preoccupation has recently generated numerous initiatives aimed at replacing these fossil sources with renewable counterparts. In particular, major efforts are being conducted in the field of polymer science and technology to prepare macromolecular materials based on renewable resources.

The aim of the present thesis was to provide a humble contribution to the ongoing research throughout the scientific community in the view of diminishing petroleum resources. Broadly, the current research work was based on the four objectives: i) making use of a renewable resource material viz; cashew nut shell liquid (CNSL) for the synthesis of monomers and polymers, ii) design and synthesis of monomers that disturb structural regularity and chain packing of the polymer backbone, iii) synthesis of processable high performance polymers, and iv) to study structure-property relationship.

Hence, the combination of phenolic character and flexible pentadecyl chain of 3-pentadecyl phenol, which in turn was obtained from CNSL-a renewable resource material- inspired a series of difunctional monomers, viz;

1. 1-Bromo-4-(4'-bromophenoxy)-2-pentadecyl benzene,
2. 4-(4'-Carboxyphenoxy)-2-pentadecylbenzoic acid,
3. 4-[4'-(Hydrazinocarbonyl)phenoxy]-2-pentadecyl benzoxydrazide,
4. 4-(4'-Aminophenoxy)-2-pentadecylbenzenamine,
5. 4-(2'-Aminophenoxy)-2-pentadecylbenzenamine,
6. 1-Isocyanato-4-(4'-isocyanatophenoxy)-2-pentadecylbenzene,
7. 1,1,1-[Bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane, and
8. 1,1-Bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane.

The most important aspect in designing of monomers was the presence of flexible linear pentadecyl chain. The existence of long alkyl chain along the polymer backbone aids in improvement in the polymer processability/solubility.

Thus, total eight difunctional monomers were designed and synthesized starting from CNSL via simple organic transformations. Of these, six monomers were synthesized for the first time.

All the monomers and intermediates involved in their synthesis were characterized by spectroscopic techniques such as FTIR and NMR spectroscopy.

These difunctional monomers were utilized for the synthesis of a variety of high performance polymers. In order to investigate the effect of incorporation of pendent pentadecyl chains on polymer properties, such as solubility, thermal transitions and heat resistance were
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evaluated. For this study, polymers such as polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters, poly(ether ketone)s and poly(ether sulfone)s were synthesized and characterized.

4-(4'-Aminophenoxy)-2-pentadecylbenzenamine was polycondensed with commercially available aromatic dialdehydes to obtain a series of (co) polyazomethines containing pendant pentadecyl chains. Inherent viscosity of (co) polyazomethines was in the range 0.50-0.70 dL/g. Medium to reasonably high molecular weight (co) polyazomethines soluble in common organic solvents such as chloroform, DCM, THF, pyridine and m-cresol were obtained. The presence of C15 alkyl chain disrupted the packing of polymer chains, as well as provided the additional ‘handle’ for interaction with solvents. Transparent and stretchable films of (co) polyazomethines derived from 4-(4'-aminophenoxy)-2-pentadecyl benzenamine with terephthaldehyde and / or isophthaldehyde could be cast from chloroform solutions. Encouraged by excellent solubility pattern of (co) polyazomethines bearing pendant pentadecyl chains, a series of copolymers by polycondensation of a mixture of 4-(4'-aminophenoxy)-2-pentadecylbenzenamine and 4,4'-oxydianiline with terephthaldehyde was prepared. However, the derived copolyazomethines were insoluble in common organic solvents. All (co) polyazomethines showed a broad halo in the wide angle region (2θ = ~ 19°). In the small-angle region (2θ = ~ 3°), a reflection was observed for all of the (co) polyazomethines. These peaks are characteristics of a typical layered structure resulting from packing of the pentadecyl side chains. T10 values obtained from TG curves for (co) polyazomethines were in the range 434-443 °C indicating their good thermal stability. Glass transition (Tg) temperature of (co) polyazomethines was evaluated by differential scanning calorimetery. All these polymers manifest a Tg value in the range 21-59 °C. The depression in glass transition temperature of (co) polyazomethines due to the presence of pendant pentadecyl chain demonstrated it’s plasticizing ability. A large difference between glass transition (21-59 °C) and initial decomposition temperature (346-380°C) was observed. This offers (co) polyazomethines a wide processing window.

New polyamides were synthesized from 4-(4'-carboxyphenoxy)-2-pentadecylbenzoic acid and aromatic diamines viz; 1,4-phenylenediamine, 1,3-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylenediamine, 4,4'-(hexafluorosilpinylidene) diaminiline and 4-(4'-aminophenoxy)-2-pentadecyl benzenamine by Yamazaki-Higashi reaction (phosphorylation reaction). The obtained polyamides had inherent viscosities in the range 0.45-0.66 dL/g and could be cast into films from DMAc solution. Most of the polyamides were soluble in polar aprotic solvents such as DMAc and NMP at room temperature or on heating. Wide angle X-ray diffraction patterns exhibited broad halo at around 2θ = ~ 19° indicating that the polymers were amorphous in nature. X-Ray diffractograms showed a reflection in the small-angle region (2θ = ~ 2-5°) for all polyamides characteristics of formation of layered structure arising from packing of pentadecyl chains. T10 values obtained from TG curves of polyamides were in the range 425-455 °C indicating good thermal stability of
polyamides. The derived polyamides showed glass transition temperatures in the range 148-189 °C. The lowering of $T_g$ could be attributed to the fact that the long alkyl chains acts as a bound solvent or internal plasticizers and also increase the free volume, thereby increasing segmental mobility, thus resulting in a reduction in the $T_g$. A large difference between glass transition (148-189 °C) and initial decomposition temperature (335-376°C) was observed which offers these polyamides a broad processing window.

A series of new poly(amideimide)s was synthesized by two-step polycondensation of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic dianhydrides viz, benzene-1,2,4,5-tetracarboxylic dianhydride or pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, 4,4'-oxydiphthalic anhydride and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. Inherent viscosities of poly(amideimide)s were in the range 0.60-0.64 dL/g indicating formation of reasonably high molecular weight polymers. Tough, transparent and flexible films of poly(amideimide)s could be cast from DMAc solutions of poly(amideimide)s. Remarkably, most of the poly(amideimide)s were found to be soluble in DMAc, NMP, pyridine and m-cresol at room temperature or upon heating. The presence of pendent flexible pentadecyl chains brought about improvement in solubility of poly(amideimide)s. Wide angle X-ray diffraction patterns of poly(amideimide)s showed broad halo at around $2\theta = \sim 19^\circ$ suggesting that all polymers were amorphous. In the small-angle region ($2\theta = \sim 3^\circ$), a reflection was observed for poly(amideimide)s. These reflections were characteristics of a layered structure resulting from the packing of the pentadecyl side chains. $T_{10}$ values obtained from TG curves were in the range of 388-410°C for poly(amideimide)s indicating their good thermal stability. Glass transition temperatures of poly(amideimide)s containing pendant pentadecyl chains and ether linkages were in the range of 162-198°C. It was observed that the plasticization effect of the attached pentadecyl side chains induced the depression of $T_g$. A large difference between glass transition (162-198°C) and initial decomposition temperature (340-356°C) was observed. This gives an opportunity for these poly(amideimide)s to be melt processed or compression molded.

A series of polyhydrazides was derived by polycondensation of 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecyl benzohydrazide and aromatic diacid chlorides viz., terephthalic acid chloride and isophthalic acid chloride. A series of polyoxadiazoles were synthesized by cyclodehydration reaction of derived polyhydrazides. Inherent viscosities of polyhydrazides and polyoxadiazoles were in the range 0.53-0.66 dL/g and 0.49 to 0.53 dL/g, respectively indicating formation of medium to reasonably high molecular weight polymers. Polyhydrazides exhibited excellent solubility in polar aprotic solvent such as DMAc, NMP, DMF and were also found to be soluble in solvents such as m-cresol and pyridine at room temperature or upon heating. Polyoxadiazoles showed solubility in polar solvents such as DMAc, NMP and DMF upon heating and even in solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine and m-cresol. The enhanced solubility could be
attributed to the flexible pentadecyl chain in the repeat unit which restricted the close packing of polymer chains and therefore allowed solvent molecules to penetrate into the polymer chains. The presence of C15 alkyl chain in polyoxadiazoles provided the additional ‘handle’ for interaction with solvents. Wide angle X-ray diffraction patterns showed that polyhydrazides and polyoxadiazoles exhibited broad halo at around $2\theta = \sim 20^\circ$ revealing an essentially amorphous nature. A strong reflection peak was observed in small angle region ($2\theta = \sim 3^\circ$) both in polyhydrazides and polyoxadiazoles indicating formation of layered structure due to the ordered packing of pentadecyl chains. Polyhydrazides showed a weight loss at around 300°C which may be attributed to the loss of water due to the thermally activated cyclodehydration reaction leading to the formation of corresponding polyoxadiazoles. $T_{10}$ values obtained from TG curves for polyoxadiazoles were in the range 433-449°C indicating their good thermal stability. A decrease in glass transition temperature was observed, both in polyhydrazides (143-166°C) and polyoxadiazoles (90-102°C) which could be ascribed to internal plasticization effect of pentadecyl chain.

A series of new aromatic polyesters was synthesized from bisphenol 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylyphenyl]ethane and aromatic diacid chlorides viz; terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) by phase transfer catalysed interfacial polycondensation technique. Since the polyester obtained from bisphenol A (BPA) and TPC is insoluble in common organic solvents, efforts were made to obtain soluble copolyesters by incorporating 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylyphenyl]ethane as a comonomer. Copolyesters were synthesized by interfacial polycondensation of BPA with TPC incorporating 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylyphenyl]ethane as a co-monomer in different proportions. Inherent viscosities of (co)polyesters were in the range 0.72-1.65 dL/g indicating formation of high molecular weight polymers. Tough, transparent and flexible films of (co) polyesters could be cast from chloroform solutions. Homopolysters and copolyesters obtained from 1,1,1-[bis-(4-hydroxyphenyl)-4'-pentadecylyphenyl]ethane exhibited good solubility in common organic solvents such as chloroform, dichloromethane, pyridine, m-cresol, etc. The presence of C15 alkyl chain disrupted the packing of polymer chains, as well as provided the additional ‘handle’ for interaction with solvents. The broad halo at $2\theta = \sim 19^\circ$ was observed for all (co)polyesters in the wide angle X-ray diffraction patterns, which could be mainly because of the presence of long pentadecyl chain, which hinders the packing of the polymer chains making them amorphous. In the small-angle region ($2\theta = \sim 3^\circ$), a reflection was observed which could be attributed the formation of layered structures due to the packing of pentadecyl side chains. $T_{10}$ values obtained from TG curves of (co) polyesters were in the range 400-460°C indicating their good thermal stability. The glass transition temperature for homopolysters were in the range 63-82°C and for copolyesters were in the range 177-183°C. All these observations clearly indicate that there is remarkable drop in glass transition temperature of polyesters by the incorporation of long pentadecyl chain which is acting as an internal plasticizer. A
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large difference between glass transition (63-183°C) and initial decomposition temperature (368-417°C) was observed. This offers (co)polyesters a wide processing window.

A series of poly(arylene ether)s viz, poly(ether ketone)s and poly(ether sulfone)s was synthesized by polycondensation of two bisphenol monomers viz, 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane containing pendant phenyl group with flexible pentadecyl chain and 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane bearing cyclohexylidene moiety with flexible pentadecyl substituent with activated aromatic dihalides. Poly(arylene ether)s were isolated as white fibrous materials with inherent viscosities in the range 0.64-1.27 dL/g indicating formation of high molecular weight polymers. Tough, transparent and flexible films could be cast from solutions of poly(arylene ether)s in chloroform. It is well known that conventional PEEK and PEKK can not be dissolved in most known organic solvents. In sharp contrast, these polymers were soluble at room temperature in common organic solvents such as chloroform, DCM, THF, pyridine and m-cresol. Most of the poly(ether ketone)s were soluble upon heating in polar aprotic solvents such as NMP, DMAc and DMF. Poly(ether sulfone)s exhibited excellent solubility pattern and were found to be soluble solvents such as chloroform, DCM, THF, DMF, DMAc, NMP, pyridine and m-cresol at room temperature or upon heating. The good solubility of the polymers could be attributed to the introduction of the pendant phenyl group with pentadecyl chain and cyclohexylidene moiety, which disturbed the close packing of the polymer chains and led to the increased free volume. The presence of C15 alkyl chain provided the additional ‘handle’ for interaction with solvents. In wide angle X-ray diffractograms, all poly(arylene ether)s exhibited a broad halo at 2θ = ~ 19°, indicating their amorphous nature. In the small-angle region (2θ = 2-3°), a reflection is observed for all poly(arylene ether)s. This indicates the formation of layered structure in poly(arylene ether)s due to the packing of pentadecyl chains. T10 values obtained from TG curves for poly(arylene ether)s were in the range 416-459 °C, indicating their good thermal stability. Poly(arylene ether)s derived from 1,1,1-[bis(4-hydroxyphenyl)-4'-pentadecylphenyl] ethane and aromatic dihalides exhibited glass transition temperature in the range 68-93°C; while, those derived from 1,1-bis(4-hydroxyphenyl)-3-pentadecyl cyclohexane showed Tg values in the range 69-95 °C. This showed that, plasticization effect of long pentadecyl chain is responsible for the substantial reduction of glass transition temperatures of poly(arylene ether)s. A large difference between glass transition (68-95°C) and polymer degradation temperature (378-417°C) was observed. This offers poly(arylene ether)s a wide processing window.

In summary, CNSL- a renewable resource material- was exploited to derive a range of new difunctional monomers via simple organic transformations. The unique feature of CNSL, i.e. the presence of C15 alkyl chain has been utilized to reduce strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect and consecutively aid in improved solubility and processability. Overall, the polymer processability / solubility was improved by the
incorporation of pendant pentadecyl chains via internal “plasticization”. The presence of C15 alkyl chain disrupted the packing of polymer chains, as well as provided the additional ‘handle’ for interaction with solvents. A large window between glass transition and polymer degradation temperature was observed. This offers polymers a wide processing window. Thus improved solubility with reasonably good thermal stability of these polymers makes them attractive materials for high performance polymers applications.

7.2 Perspectives

The present work on design and synthesis of difunctional monomers starting from CNSL and processable high performance/ high temperature polymers has opened up many prospects for the future work.

- The present work on the synthesis of difunctional monomers starting from CNSL- an inexpensive and abundantly available renewable resource material- has expanded the range of condensation monomers available for the preparation of high performance polymers with improved processability.

- The dibromo compound viz, 1-bromo-4-(4' -bromophenoxy)-2-pentadecyl benzene synthesized in the present work is a potentially useful monomer for synthesis of polyamides and polyesters by transition metal-catalyzed carbonylative coupling with diamines and diphenols, respectively.

- 1-Bromo-4-(4' -bromophenoxy)-2-pentadecyl benzene could easily be converted into corresponding diphenol and dildehyde, which by themselves represent valuable monomers for synthesis of a host of high performance polymers.

- The difunctional monomers synthesized in the present work are unsymmetrical and the difference in reactivity of the two functional groups arises due to steric factors. It would be interesting to systematically investigate the constitutional isomerism in the polymers derived from such monomers and examine its influence on the polymer properties.

- It would now be interesting to synthesize other step-growth polymers based on synthesized difunctional monomers. For example, aromatic diisocyanate containing pendant pentadecyl chain is a potentially useful monomer for the synthesis of polyurethanes and polyureas.

- The primary focus of the present work was to illustrate the influence of pendant pentadecyl chains on the solubility behavior and thermal properties of polyazomethines, polyamides, poly(amideimide)s, polyhydrazides, polyoxadiazoles, polyesters and poly(arylene ether)s. Detailed studies using variable temperature WAXD and $^{13}$C solid-state NMR spectroscopy would yield useful information on the packing mode and conformational transitions of the pentadecyl side chains.
High performance/ high temperature polymers synthesized in the present work could be cast into tough and flexible films from solution in organic solvents. It would be worthwhile to evaluate some selected polymers as membrane materials for gas separation studies.