Synthesis of (2,7-dibromo-9,9-dialkyl-substituted-fluorene)s for Poly(dialkylfluorene)s by Phase Transfer Catalytic Reaction

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Abstract

2,7-dibromo-9,9-dialkyl-substituted-fluorene derivatives were prepared by the alkylation of 2,7-dibromofluorene with various alkyl groups under two-phase phase transfer catalysis (PTC) conditions, as monomers for synthesizing poly(dialkylfluorene)s. Tetra-n-butylammonium hydrogen sulfate (TBAHS) was used as a phase transfer catalyst to enhance nucleophilic substitution. In addition, NaOH in water (25M) was used as a base to generate anions. Compared to conventional alkylation using butyllithium(BuLi), the reaction using the PTC technique attained high selectivity and substantial conversion of reactants, due to the enhanced reaction rate, while the reaction was carried out under moderate conditions. An approximately 90% yield was obtained from the reaction and the reaction time was remarkably reduced. 2,7-dibromo-9,9-dihexyl-fluorene, 2,7-dibromo-9,9-dioctyl-fluorene, and 2,7-dibromo-9,9-di(2-ethylhexyl)-fluorene were effectively synthesized by phase transfer catalytic reaction.

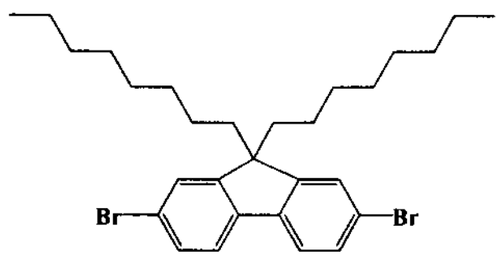
1. Introduction

Poly(alkylfluorene)s are promising new materials for polymer light-emitting diodes (PLEDs) due to their photoluminescence (PL) quantum efficiencies and thermal stability [1]. The fluorene structural unit provides rigid planar biphenyl units in the polymer backbone, which offers mechanical and chemical stability without inducing significant torsional strain that would adversely affect conjugation. Moreover, the facility of substitution at the C-9 position of the monomeric fluorene allows control of the polymer properties, such as solubility, processibility, and morphology [2, 3]. Substituted poly(dialkylfluorene) derivatives have been prepared by oxidative polymerization of 9,9-dialkyl-substituted monomers, such as by nickel-catalyzed reductive polymerization [4] or by using the Suzuki coupling reaction [5]. In these polymers, dialkyl side groups function to solvate ions and to promote ion transport, while the conjugated poly(1,4-phenylene) main chain is capable of transporting electrons and holes [6].

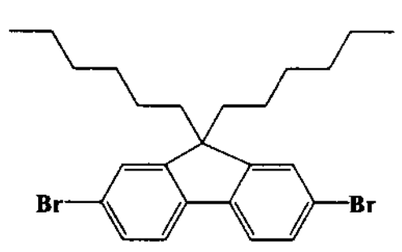
In order to prepare poly(9,9-dialkyl-substituted fluorene)s, initially, (2,7-dibromo-9,9-dialkyl-substituted-fluorene)s should be synthesized as monomers. In most case, these monomers have been synthesized by alkylation using n-BuLi and by bromination [4, 6, 7]. However, in this case, the necessary repeated substitutions with BuLi and alkyl halide and multiple purifications, such as by vacuum distillation and column chromatography, lead to reduced product yield and increased reaction time. In addition, it is difficult to control the reaction due to the very low temperature used, below –40°C. In order to simplify the synthetic route for obtaining monomers, (2,7-dibromo-9,9-dialkyl-substituted-fluorene)s, these can be synthesized by a phase transfer catalytic reaction in a two-phase solution. Phase transfer catalysis (PTC) is an effective mechanism for synthesizing organic chemicals from two immiscible reactants, such as in the case of substitution, C- and O-alkylation, oxidation and dichloroproponation. The main advantages of using the PTC technique to synthesize organic chemicals are the enhanced reaction rate, the possibility of carrying out the reaction at moderate conditions, the high selectivity with which the main product is obtained and the high conversion rate of the reactants [8]. Liquid-liquid PTC is the reaction between a lipophilic substrate, dissolved in an organic phase, and a hypophilic reactant solubilized in water [9]. In this reaction, quaternary salts are usually used as phase transfer catalysts in order to enhance the reaction rate; for example tetra-*n*-butylammonium bromide(TBAB), tetra-*n*-butylammonium hydrogen sulfate(TBAHS), tetra-*n*-butylammonium hydroxide(TBAOH), tetra-*n*-butylammonium iodide(TBAI), and tetra-*n*-butylphosphonium bromide(TBPB) [10]. Because the reaction of the 2,7-dihalofluorene with hydrocarbyl halide is an interfacial process using phase transfer catalysts, (2,7-dibromo-9,9-dialkyl-substituted-fluorene)s with various side chains can effectively be synthesized using a phase transfer catalytic reaction.

In this study, (2,7-dibromo-9,9-dialkyl-substituted-fluorene)s were synthesized with both 2,7-dibrominated fluorene and alkyl side groups, such as hexyl, octyl, and 2-ehtylhexyl functional groups, using a phase transfer catalytic reaction in a two-phase solution. The mechanism and process conditions for the reaction were investigated,

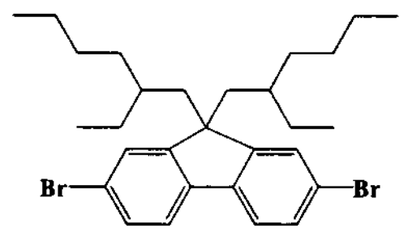
in order to obtain products with high purity and yield. Figure 1 shows the schematic diagrams of synthesized 2,7-dibromo-9,9-dialkyl-substituted fluorenes.



(a)



(b)



(c)

Figure 1. Schematic diagrams of (a)2,7-dibromo 9,9dioctyl fluorene, (b) 2,7-dihexyl-9,9-dioctyl-fluorene, and (c) 2,7-dibromo-9,9-di(2-ethylhexyl)-fluorene

2. Experimental

2.1 Synthesis of 2,7-dibromo- 9,9-dioctyl-fluorene

To a solution of brominated fluorene (8.1g), 2,7-dibromofluorene, in toluene (90ml), 1-bromooctane (9.64g) and tetra-*n*-butylammonium hydrogen sulfate (TBAHS, 0.534g) were added. Then, this solution was mixed with 50wt% aqueous NaOH solution (90ml). The resulting heterogeneous mixture was uniformly stirred and heated at 80°C for 25minutes until all the starting material had been consumed (TLC monitoring). After cooling, the solution was separated and the organic portion of the solution was washed by an alkaline solution (10 wt% aqueous NaCl solution) at least three times to remove TBAHS, and then dried over $MgSO_4$. The solvent was concentrated using a rotary vacuum evaporator. The resultant material was purified by recrystallization from methanol. A yellowish solid of a high purity was obtained. The product was identified by GC mass for molecular weight and ^{1}H NMR for functional group.

2.2 Synthesis of 2,7-dibromo-9,9-dihexyl-fluorene

To a solution of brominated fluorene (8.1g), 2,7-dibromofluorene, in toluene (90ml), 1-bromohexane (8.32g) and tetra-*n*-butylammonium hydrogen sulfate (TBAHS, 0.534g) were added. Then, this solution was mixed with 50wt% aqueous NaOH solution (90ml). The resulting heterogeneous mixture was uniformly stirred and heated at 80°C for 30 minutes until all the starting material had been consumed (TLC monitoring). After cooling, the solution was separated and the organic portion of the solution was washed by an alkaline solution (10 wt% aqueous NaCl solution) at least three times to remove TBAHS, and then dried over $MgSO_4$. The solvent was concentrated using a rotary vacuum evaporator. The resultant material was purified by recrystallization from methanol. A yellowish solid of a high purity was obtained. The product was identified by GC mass for molecular weight and ^{1}H NMR for functional group.

2.3 Synthesis of 2,7-dibromo-9,9-di(2-ethylhexyl)-dibromofluorene

To a solution of brominated fluorene (8.1g), 2,7-dibromofluorene, in toluene (90ml), 2-ethylhexyl bromide (9.64g) and tetra-*n*-butylammonium hydrogen sulfate (TBAHS, 0.534g) were added. Then, this solution was mixed with 50wt% aqueous NaOH solution (90ml). The resulting heterogeneous mixture was uniformly stirred and heated at 80°C for 45minutes until all the starting material had been consumed (TLC monitoring). After cooling, the solution was separated and the organic portion of the solution was washed by an alkaline solution (10wt% aqueous NaCl solution) at least three times to remove TBAHS, and then dried over $MgSO_4$. The solvent was concentrated using a rotary vacuum evaporator. The resultant material was purified by silica gel column chromatography. A yellowish viscous liquid of high purity was obtained. The product was identified by GC mass for molecular weight and ^{1}H NMR for functional group.

3. Results and Discussion

Phase transfer catalysis (PTC) usually involves carrying out the reaction in a two-phase system. One part of the molecule is soluble in polar solvents, while the other part is soluble in water. When an aqueous NaOH solution is mixed with a solution of 2,7-dibromofluorene and an alkyl halide such as 1-bromohexane, 1-bromooctane, and 2-ethylhexyl bromide in toluene, as the water-insoluble organic solvent, two layers result. Reaction can occur only at the interface of these layers, so that the reaction is very slow. Tetra-n-butylammonium hydrogen sulfate (TBAHS) was used as a phase transfer catalyst, in order to transfer OH^- ions to the organic solution, so that the reaction could occur in the organic solution as well as at the interface. (n-$C_4H_9)_4N^+$ ions from TBAHS are able to partition the anions between the two phases, because the cation, (n-$C_4H_9)_4N^+$, can form an ion pair with many different anions. Because the ion pair is a salt, it will normally be water-soluble. Also, due to the presence of the carbon atoms in (n-$C_4H_9)_4N^+$, its ion pair will be also soluble in organic

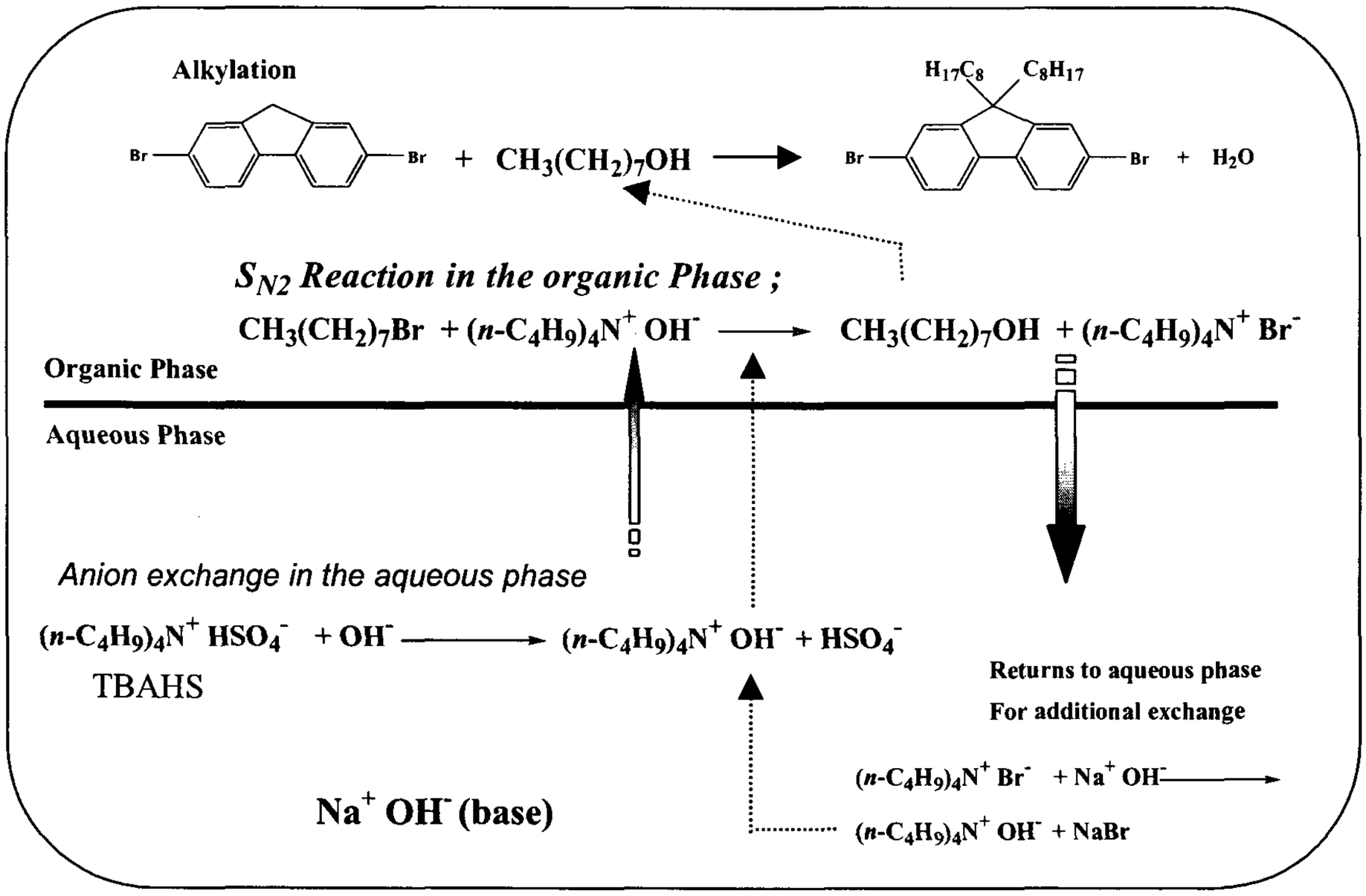


Figure 2. Schematic diagram of phase transfer catalytic cycle of 2,7-dibromo-9,9-dioctyl-fluorene.

solvents. Therefore, the reaction is much faster, since nucleophiles such as OH- and CN- are more nucleophilic and more reactive when they are not solvated by water. The catalytic action of $(n\text{-}C_4H_9)_4N^+$ HSO_4^- arises from the fact that it is water soluble and also slightly soluble in organic solvents, thus influencing the reaction rate. If the aqueous layer contains an excess of OH^- ions, the salt can be transferred into the organic layer as mainly $(n\text{-}C_4H_9)_4N^+$ OH^-, not $(C_4H_9)_4N^+$ HSO4-. Thus, the salts of the nucleophile are usually used in high concentration in the aqueous solution [11]. Figure 2 shows the reaction mechanism for 2,7-dibromo-9,9-dioctyl-fluorene by phase transfer catalysis.

Initially, anion exchange in the aqueous phase occurs to form the salt, $(n\text{-}C_4H_9)_4N^+$ OH^-. This salt is transferred into the organic phase and reacts with 1-bomooctane $[CH_3(CH_2)_7Br]$. As a result, $CH_3(CH_2)_7OH$, and $(n\text{-}C_4H_9)_4N^+$ Br^- are formed by S_{N2} reaction. The $(n\text{-}C_4H_9)_4N^+$ Br^- returns to the aqueous phase for additional exchange, and $CH_3(CH_2)_7OH$ reacts with 2,7-dibromofluorene to form 2,7-dibromo-9,9-dioctyl-fluorene. This phase transfer catalytic cycle takes place repeatedly.

Generally, the reactivity of phase transfer catalysis (PTC) is controlled by reaction temperature, base concentration, and phase transfer catalyst concentration.

Moreover, it is very important to select a proper quaternary salt, because the phase transfer of the anion influences the reaction in PTC. Polar solvents such as dichloromethane, 1,2-dichloroethane, chloroform, toluene, and *n*-hexane are normally used as the water-insoluble solvents in PTC. It has been reported that dichloromethane and chlorobenzene are often used in PTC, because the organic reaction rate increases with increasing solvent polarity [10]. However, in this study, toluene was used as the organic solvent, since it dissolved both reactants well (2,7-dibromofluorene and alkyl halides). In addition, base concentration also influences and determines the PTC reaction rate. In this study, a NaOH solution with a concentration of 25M was used as a saturated aqueous solution, in order to form an excess of OH^- ions. In order to control the reaction rate, since the functional groups of quaternary salts also influence the dissolution of the catalyst in the organic phase, it is necessary to properly select the phase transfer catalyst. There is no universal rule for selecting an appropriate catalyst; this only can be found by experiment. The reason for this is that different reactions need different catalysts, in order to increase their rate and to improve their yield under any one set of conditions. Here, tetra-n-butylammonium hydrogen sulfate (TBAHS) was used due to its relatively high solubility in toluene. The reaction temperature is also an important factor for determining the reaction rate. In this experiment, the PTC reaction did not take place well below 60°C. At 60 ~ 75°C,

the reaction rate was relatively slow. Furthermore, the conversion rate of the reactants was low. Reaction temperature was optimized at 75 ~80°C within 40 minutes. Approximately 90% yield was obtained in all cases of substitution with hexyl, octyl, and 2-ethylhexyl groups. However, side reactions like gel formation were observed over 80°C.

Figures 3, 4, and 5 show the results of ^{1}H NMR of 2,7-dibromo-9,9-dioctyl-fluorene, 2,7-dibromo-9,9-dihexyl-fluorene and 2,7-dibromo-9,9-di(2-ethylhexyl)-fluorene, respectively, synthesized under the above reaction conditions.

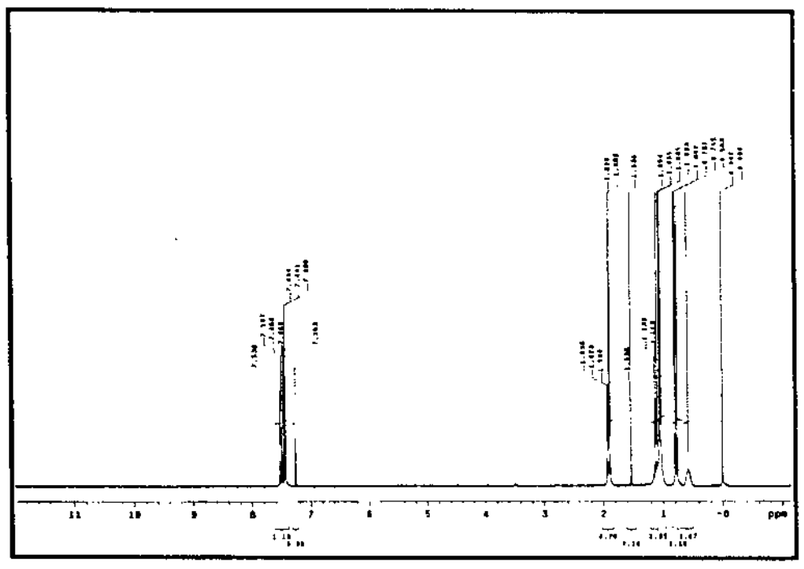


Figure 3. ^{1}H NMR spectrum (300MHz) of 2,7-dibromo-9,9-dioctyl-fluorene in $CDCl_3$.

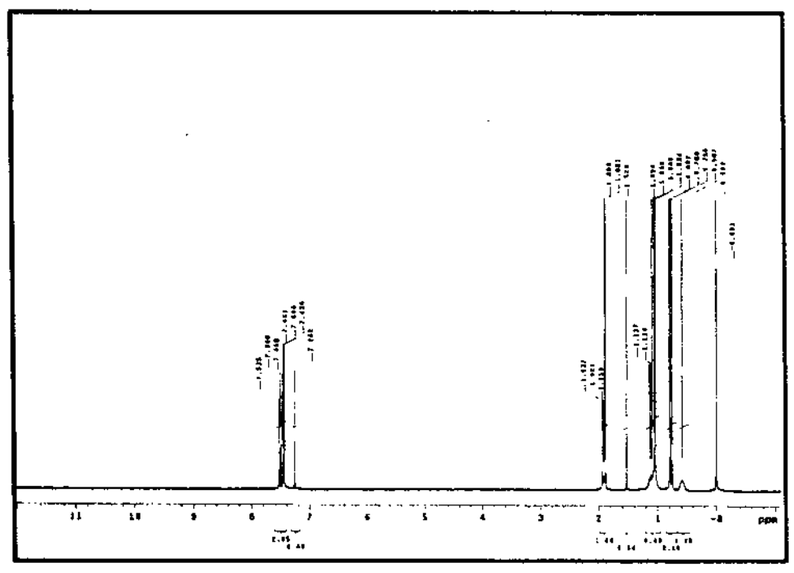


Figure 4. ^{1}H NMR spectrum (300MHz) of 2,7-dihexyl-9,9-dioctyl-fluorene in $CDCl_3$

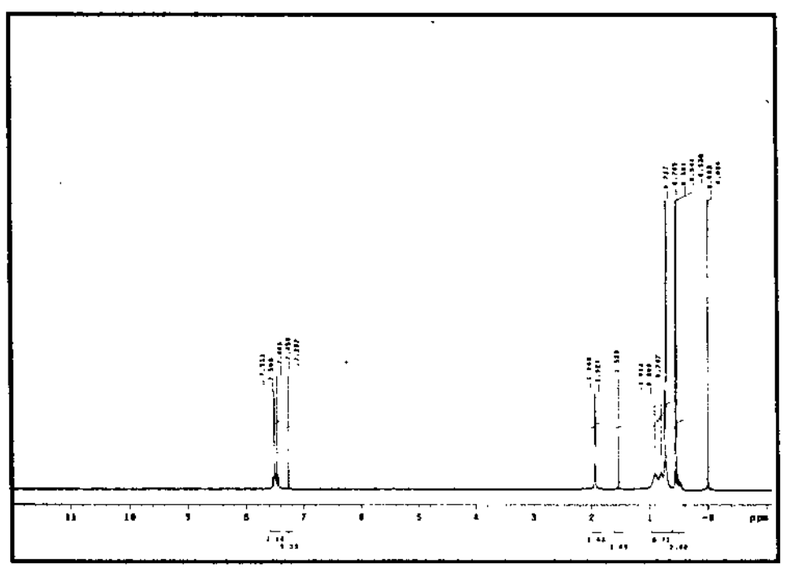


Figure 5. ^{1}H NMR spectrum (300MHz) of 2,7-dibromo-9,9-di(2-ethylhexyl)-fluorene in $CDCl_3$

4. Summary

In summary, (2,7-dibromo -9,9-dialkyl-substituted-fluorene)s were prepared with octyl, hexyl, and 2-ethylhexyl groups, under phase transfer catalysis conditions, as monomers for synthesizing poly(dialkylfluorene)s. The PTC technique was found to be very effective in comparison with the conventional method using BuLi in that high selectivity and high reactant conversion was obtained, using a simple and easy to perform reaction process with a relatively short reaction time. In addition, dialkyl-substituted monomers can easily be synthesized with various alkyl groups for poly(dialkylfluorene)s applications

5. References

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6. Acknowledgements

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