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New Fluorene Containing Monomers and Polymers

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SUMMARY

The synthesis of five novel electrono-donor monomers containing fluorene (2-fluorenyl acrylamide, 2-fluorenyl methacrylamide, 2-(1-hydroxyethyl)fluorenyl acrylate, 2-(1-hydroxyethyl)fluorenyl methacrylate and 9-fluorenyl acrylate) and of the corresponding polymers is described.

INTRODUCTION

The constantly increasing interest on aromatic group containing monomers and polymers started particulary when the charge transfer complex: poly(N-vinylcarbazole)-2,4,7-trinitro-9-fluorenone was used as a photoconductor in electrophotography (SCHAFFERT 1971). Of aromatic compounds, the only one which permits the synthesis of both electrono-donor and electrono-acceptor monomers is fluorene (PEARSON 1977). This is one of the reasons why, recently, besides the study of 2-vinylfluorene polymerization and copolymerization (GIPSTEIN et al. 1972, COHEN and MARECHAL 1975), attention was directed to synthesis and polymerization of new monomers containing fluorene: 2-vinyl-9-fluorenone (YANUS and PEARSON 1974), 2-vinyl fluorenyl ether and 2,7-divinyl fluorenyl ether (LEVCHENKO et al.1975) allyl-9-fluorenyl ether (AKPEROV and DZHAFAROVA 1975), N-(2-fluorenyl)maleimide (OISHI and KIMURA 1976), 2,4,7-trinitro-9-fluorenyl methacrylate (TURNER and AUCLAIR 1976), 9-fluorenyl propiolate and 2,4,7-trinitro-9-fluorenyl propiolate (SIMIONESCU et al. 1979). This paper is dealing with the synthesis and polymerization of five new fluorene containing monomers: 2-fluorenyl acrylamide, 2-fluorenyl methacrylamide, 9-fluorenyl acrylate, 2-(1-hydroxyethyl)fluorenyl acrylate, 2-(1-hydroxyethyl)fluorenyl methacrylate, and with a new method for the synthesis of 9-fluorenyl methacrylate (NISHINO et al. 1971).

EXPERIMENTAL

The monomers were synthesized according to the reactions presented in Scheme 1. The intermediary derivatives (2-aminofluorene, 9-diazofluorene, 2-(1-hydroxy-

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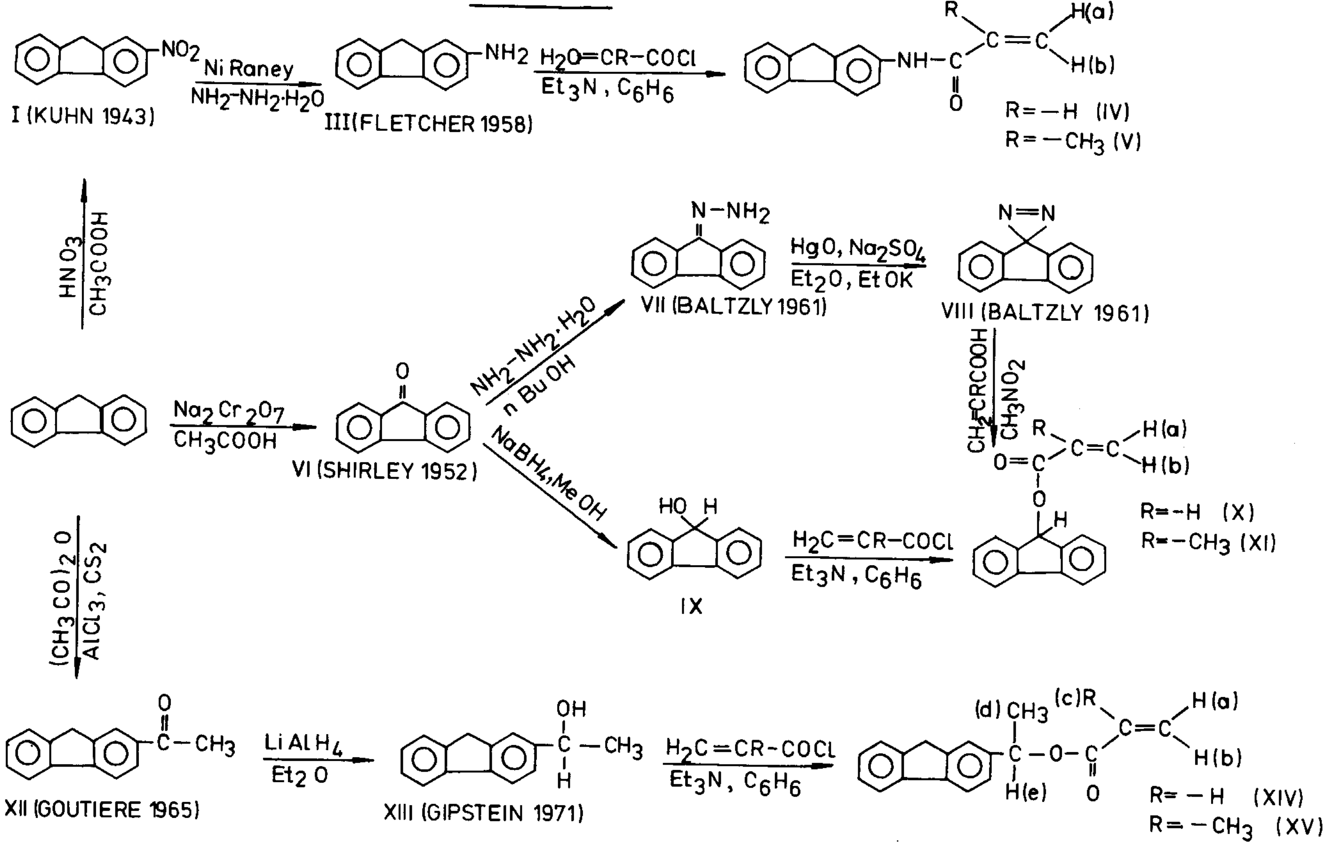
SCHEME 1


I (KUHN 1943)

III(FLETCHER 1958)

R= —H (IV)
R= —CH$_3$ (V)

VI (SHIRLEY 1952)

VII (BALTZLY 1961)

VIII (BALTZLY 1961)

IX

R=-H (X)
R=-CH$_3$ (XI)

XII (GOUTIERE 1965)

XIII (GIPSTEIN 1971)

R= —H (XIV)
R= —CH$_3$ (XV)

ethyl)fluorene) were synthesized according to literature data (in parenthesis) in Scheme 1. 9-Hydroxyfluorene was obtained by the reduction of 9-fluorenone with $NaBH_4$.

9-Hydroxyfluorene (IX). A solution of 5 g $NaBH_4$ in 50 ml of 0.4 N NaOH was added dropwise to a stirred mixture of 36 g (0.2 moles) of VI in 800 ml of methanol. The mixture turned into a clear colourless solution, which was stirred below its boiling point for 1 hr. On cooling, the solution afforded white crystals. The product was filtered, washed with water, dried and recrystallized from methanol to provide 35.0 g (95%) of white crystals, m.p. 197°C (KERP 1896, m.p. 196°C). Its structure was proved by elemental analysis, IR and NMR, to correspond with that of 9-hydroxyfluorene.

2-Fluorenyl acrylamide (IV). A mixture of 2.09 g (0.023 moles) acryloyl chloride and 10 ml benzene was added dropwise (during 20 minutes) under vigorous stirring to a solution (cooled to 8°C) of 3.62 g (0.02 moles) of 2-aminofluorene, 150 ml benzene and 2.02 g (0.023 moles) triethylamine (TEA). The mixture was stirred for one hr. at 10°C and 2 hrs. at room temperature. The obtained suspension was succesively washed with water (to remove $Et_3N.HCl$), NaOH (5% water solution), water, and then dried over anhydrous $CaCl_2$. After removing benzene in vacuo below 30°C, the product was recrystallized from methanol to provide 3.1 g (61.6%) of white crystals, m.p. 170-171°C.

ANAL.Calcd.for $C_{16}NO_2H_{13}$(251.272): C, 76.47%; N, 5.57% O, 12.74%; H, 5.22%. Found: C, 76.30%; N, 5.65%; H, 5.15%.

IR(KBr): 3270 (νNH); 1660 (secondary amide group I); 1540 (secondary amide group II); 1600 (νC=C); 1410 (ν=CH in plane); 985 (ν=CH out of plane I); 965 (ν=CH out of plane II); 768 and 732 cm^{-1} (fluorenyl group).

NMR($CDCl_3$): δ = 3.68(s, 2H, methylenic fluorenyl group) δ= 5.45-6.40(m, 3H, vinyl group) and δ = 7.0-7.9(m, 7H fluorenyl group).

2-Fluorenyl methacrylamide (V). 3.9 g (76.31%) of light-brown crystals, m.p. 157-158°C, were obtained in the same way as compound IV, except that acryloyl chloride was changed with methacryloyl chloride.

ANAL.Calcd.for $C_{17}NO_2H_{15}$(265.298): C, 76.96%; N, 5.28% O, 12.06%; H, 5.70%. Found: C, 77.40%; N, 5.33%; H, 5.65%.

IR(KBr): 3300(νNH); 1655(secondary amide group I); 1525(secondary amide group II); 1620(νC=C); 925(ν=CH out of plane); 770 and 739 cm^{-1}(fluorenyl group).

NMR($CDCl_3$): δ = 1.95(s, 3H, $-CH_3$); δ= 3.68(s, 2H, methylenic fluorenyl group); δ = 5.26(s, 1H, =CHa); δ= 5.61(s, 1H, =CHb); δ = 7.0-7.8(m, 7H, fluorenyl).

9-Fluorenyl acrylate (X) from (VIII). About 4.2 ml of freshly distilled acrylic acid was added dropwise to a stirred mixture of 2.49 g (0.013 moles) of 9-diazo-

fluorene and 25 ml of nitromethane. Gas evolution (nitrogen) was noted during the reaction. After about 20 minutes, a clear red solution was obtained. The solvent was evaporated below 50°C, and the obtained oil phase was succesively washed with water and stirred until solidification. The dried product was chromatographed on Al_2O_3 (eluent: n-pentane), and the solvent was then removed at a temperature below 30°C. On staying in the refrigerator, the oil phase crystallized. The product was recrystallized from methanol/water = 1/1 mixture to provide 0.8 g (26%) of light-yellow crystals, m.p. 60°C.
ANAL.Calcd.for $C_{16}O_2H_{12}$(236.256): C, 81.34%; O, 13.54 %; H, 5.12%. Found: C, 81.95%; H, 4.97%.
IR(KBr): 1705(νC=O); 1620(νC=C); 1394(ν=CH in plane); 968(ν=CH out of plane I); 840(ν=CH out of plane II); 755, 750, 733 and 720 cm^{-1}(fluorenyl).
NMR($CDCl_3$): δ= 5.67-6.90(m, 3H, vinyl); δ= 6.83(s, 1H, methynic fluorenyl); δ= 7.0-7.7(m, 8H, fluorenyl).
9-Fluorenyl methacrylate (XI) from (VIII), was synthesized in the same way as compound X (30%), m.p. 62°C.
ANAL.Calcd.for $C_{17}O_2H_{14}$(250.282): C, 81.58%; O, 12.78 %; H, 5.64%. Found: C, 82.07%; H, 5.50%.
IR(KBr): 1704(νC=O); 1620(νC=C); 842(ν=CH out of plane); 755, 735, 728 and 719 cm^{-1}(fluorenyl).
NMR($CDCl_3$): δ= 2.0(s, 3H, $-CH_3$); δ= 5.5(s, 1H, =CHa); δ= 6.07(s, 1H, =CHb); δ= 6.78(s, 1H, methynic fluorenyl); δ= 7.0-7.65(m, 8H, fluorenyl).
9-Fluorenyl acrylate (X) from (IX), was synthesized by the same method as the product (IV), from 10 g (0.055 moles) of 9-hydroxyfluorene, 300 ml of benzene, 11.13 g (0.11 moles) of TEA and 10 g (0.11 moles) of acryloyl chloride. The reaction was carried out for 10 hrs. at room temperature. After the solvent was evaporated, only two recrystallizations from methanol/water = 1/1 mixture were enough to obtain 5.5 g (41.82%) of a high purity compound X.
9-Fluorenyl methacrylate (XI) from (IX), was synthesized with a 95% yield by the above described procedure.
2-(1-Hydroxyethyl)fluorenyl acrylate (XIV). It was prepared by the same procedure as compound IV, from 17 g (0.081 moles) of 2-(1-hydroxyethyl)fluorene, 1500 ml of benzene, 14.51 g (0.143 moles) of TEA and 13 g (0.143 moles) of acryloyl chloride. The reaction was carried out for 10 hrs. at room temperature and then left overnight. The methanol recrystallization of the remained product after benzene evaporation afforded 7.5 g (35%) of white crystals, m.p. 64-65°C. When the reaction was carried out with a low excess of acryloyl chloride (vs. XIII) and a low reaction time, the yield was very low, and the reaction products could be separated by column chromatography only (Al_2O_3, ethylic ether/petroleum ether = 3/1, eluent).

ANAL.Calcd.for $C_{18}O_2H_{16}$(264.308): C, 81.79; O, 12.11%; H, 6.10%; Found: C, 82.30%; H, 5.92%.
IR(KBr): 1710(νC=O); 1620(νC=C); 1392(ν=CH in plane); 980(ν=CH out of plane I); 828(ν=CH out of plane II); 766 and 732 cm^{-1} (fluorenyl).
NMR($CDCl_3$): δ= 1.56(d, 3H, $-CH_3$d); J_{de} = 6 Hz; δ= 3.78(s, 2H, methylenic fluorene); δ= 5.55-6.50(m, 4H, -He and vinyl); δ= 7.1-7.8(m, 7H, fluorenyl).
2-(1-Hydroxyethyl)fluorenyl methacrylate (XV), was synthesized by the same procedure as compound XIV, (44.5%) m.p. 68-69°C.
ANAL.Calcd.for $C_{19}O_2H_{18}$(278.334): C, 81.98%; O, 11.50% H, 6.52%. Found: C, 82.20%; H, 6.45%.
IR(KBr): 1700(νC=O); 1624(νC=C); 840(ν=CH out of plane); 766 and 732 cm^{-1} (fluorenyl).
NMR($CDCl_3$): δ= 1.62(d, 3H, $-CH_3$d); J_{de} = 6 Hz; δ= 1.975(s, 3H, $-CH_3$c); δ= 3.85(s, 2H, methylenic fluorenyl); δ = 5.51(s, 1H, -Ha); δ= 6.11(s, 1H, -Hb); δ= 5.95(q, 1H, -He); δ= 7.1-7.8(m, 7H, fluorenyl).
Polymerization of monomers. All monomers synthesized were subjected to a free-radical solution (20% in dioxane, 60°C) polymerization procedure, which consists in the use of 1% of α,α'-azobisisobutyronitrile, based on the weight of monomer, as initiator, in a sealed ampoule and air-free conditions. Polymers were separated by precipitation with methanol. Intrinsic viscosities were measured in tetrahydrofuran at 25°C.

DISCUSSION

The synthesized monomers polymerize easily by radical mechanism (Table 1). All polymers thus prepared show the same characteristic IR absorption bands as the respective monomer, except that the vinyl absorptions are absent. The ^{1}H-NMR chemical shifts of these polymers are presented in Table 1.

TABLE 1

Results of radical polymerization of monomers (reaction time 27 hrs.) and chemical shifts (solvent $CDCl_3$, for poly(IV) - $(CD_3)_2SO$, 60°C) of ^{1}H-NMR polymer spectra

Monomer	Conversion[%]	[η] [dl/g]	Chemical shifts of ^{1}H-NMR polymer spectra
IV	63.06	0.09	7.08(7H aromatic); 3.35(2H, metylenic fluorenyl); 2.0(2H,$-CH_2-$)
V	26.42	0.11	7.0(7H aromatic); 3.3(2H, methylenic fluorenyl); 2.45(2H,$-CH_2-$) 1.4(3H, $-CH_3$)
X	51.76	0.15	7.1(8H aromatic); 6.46(2H, methylenic fluorenyl); 2.6(1H,-CH-) 1.7(2H,$-CH_2$)
XI	60.60	0.12	7.28(8H, aromatic); 6.38(1H, methynic fluorenyl); 2.18(2H,$-CH_2-$) 1.27(3H,$-CH_3$)

Table 1 - continued

XIV	23.44	0.18	7.15(7H aromatic); 5.7(1H,-He); 3.6(2H, methylenic fluorenyl); 2.3(1H,-CH-); 2.0(2H,-CH$_2$-); 1.4(3H,-CH$_3$d)
XV	66.20	0.10	7.2(7H aromatic); 5.4(1H,-He); 3.65(2H, methylenic fluorenyl); 1.86(2H,-CH$_2$-); 1.25(3H,-CH$_3$d); 0.7(3H,-CH$_3$c)

The polymers are soluble in aromatic solvents, halogenated solvents, dioxane, tetrahydrofuran, dimethylformamide, dimethylsulfoxid, except poly(IV), which is not soluble in aromatic and halogenated solvents.

REFERENCES

AKPEROV, O. G. and DZHAFAROVA, E. A.: Vysokomol. Soed. B17, 81 (1975)
BALTZLY, R., MEHTA, N. B., RUSSEL, P. B., BROOKS, R. E., GRIVSKY, E. M. and STEINBERG, A. M.: J. Org. Chem. 26, 3669 (1961)
COHEN, S. and MARECHAL, E.: J. Polym. Sci.,Symp. 52, 83 (1975)
FLETCHER, T. L.: J. Org. Chem. 23, 680 (1958)
GIPSTEIN, E., HEWETT, W. A. and NEED, O. U.: J. Polym. Sci. Polym. Lett. Ed. 9, 671 (1971)
GOUTIERE, G. and GOLI, J.: Bull. Soc. Chim. Fr. 1, 1962 (1965)
KERP, W.: Ann. 29, 228 (1896)
KUHN, W. E.: Org. Syn. Coll. Vol. II, 447 (1943)
LEVCHENKO, A. I., SHISHKINA, N. I. and PLIEV, T. N.: Vysokomol. Soed. B17, 313 (1975)
MARSH, D. G., YANUS, J. F. and PEARSON, J. M.: Macromolecules 8, 427 (1975)
NISHINO, J., NAKAHATA, H. and SAKAGUCHI, Y.: Polymer J. 2, 555 (1971)
OISHI, T. and KIMURA, T.: Kobunshi Ronbunshu 33, 141 (1976)
PEARSON, J. M.: Pure Appl. Chem. 49, 463 (1977)
SCHAFFERT, R. M.: IBM J. Res. Dev. 15, 75 (1971)
SHIRLEY, D. A.: Preparation of Organic Intermediates, New York: Wiley, 1952
SIMIONESCU, C. I., DUMITRESCU, S., GRIGORAS, M. and PERCEC, V.: J. Polym. Sci. Polym. Lett. Ed. 17, 287 (1979)
TURNER, S. R. and AUCLAIR, C.: Macromolecules 9, 868 (1976)
YANUS, J. F. and PEARSON J. M.: Macromolecules 7, 716, 951 (1974)

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