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Transformation of C≡C Triple Bond of Poly(aryleneethynylene) Type Polymers to C=C Double Bond

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C≡C triple bond of poly(aryleneethynylene) type polymer is converted to C=C double bond by the reaction with HBr, and the =C-Br group thus formed is further transformed to an ester group.

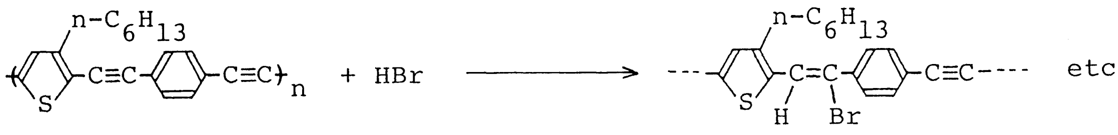
Electrical and optical properties of π-conjugated polymers is the subject of recent interest. Poly(arylenevinylene) PAV type polymers belong to a class of polymers most widely studied on their optical properties.[1)] In addition to the PAV type polymers, poly(aryleneethynylene) PAE type polymers have been obtained with various combinations of Ar and Ar' groups.[2)]

-(Ar-CH=CH)-_n $\quad$ $\text{-(Ar-C≡C-Ar'-C≡C)-}_n$

PAV $\quad$ PAE

Since the C≡C bond has high reactivity toward various reactants, transformation of the C≡C bond of the PAE type polymers to C=C bond is expected to give a series of new π-conjugated polymers. However, such transformation has not been reported. As the first step to develop such transformation reactions, we now report addition reaction of HBr to recently reported soluble PAE type polymers.[2a)]

Reaction of the following polymer (PAE-TP)[2)] with excess dry HBr (ca. 20 mol/mol of C≡C bond) smoothly proceeds in benzene at room temperature, although the possibility that the reaction is accompanied with partial decomposition of the thiophene ring is not excluded.[3)] The fairly strong ν(C≡C) band in the IR spectrum of PAE-TP is considerably weakened in the IR spectrum of the HBr-added polymer obtained after the reaction time of



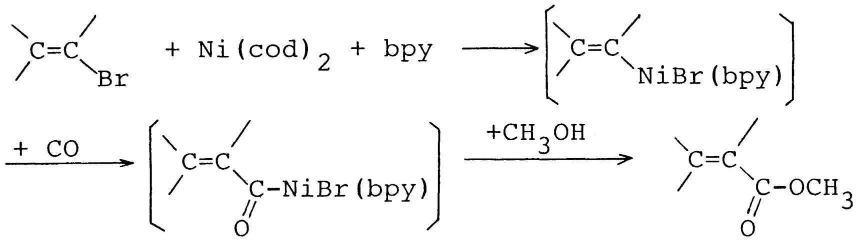
PAE-TP

(1)

30 min. Analysis of Br (19.8%) of the HBr-added product indicates addition of 0.25 g of Br to 1.0 g of PAE-TP corresponding to 0.91 mol of HBr per 1 mol of the repeating unit of PAE-TP.

^{1}H-NMR spectrum of the HBr-added polymer shows overlapped signals of the aromatic and olefinic protons in a range of δ6.7-8.0 ppm in CD_2Cl_2; relative area of the signals in the range against that of hexyl group (relative area = 13) increases 5 of PAE-TP to about 6 after the HBr addition. A similar reaction (30 min at room temperature) of another PAE type polymer (Ar = p-phenylene; Ar' = 2-phenyl-p-phenylene) with HBr also proceeds to cause addition of about 1 mol of HBr per its repeating unit.

The =C-Br group formed can be further converted to an ester group by treatment with excess amounts of Ni(0) complex (a 1:1.1 mixture of bis(1,5-cyclooctadiene)nickel(0) (about 4 mol/mol of the C-Br bond) and 2,2'-bipyridine bpy) and carbon monoxide (1 atm) in THF at room temperature followed by treatment of the reaction mixture with excess CH_3OH in a manner similar to that previously reported for the conversion of Cl of poly(vinyl chloride) to the ester group.[4)]



The ester group thus formed gives rise to a fairly strong ν(C=O) band at 1720 cm^{-1}. Transformation of the =C-Br group to amide[4,5)] was also possible by using aniline instead of methanol in the above reaction.

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References

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3) GPC analysis (polystyrene standard) suggests decrease in molecular weight of PAE-TP[2a)] by 21% after the reaction with HBr, which may be attributed to the decomposition of the thiophene ring.
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