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Novel polycondensation catalyzed by a palladium complex

I. Polymer synthesis using the coupling reaction between aryl halide and acrylate

Masato Suzuki, Katsuhiko Sho, Jong-Chan Lim, and Takeo Saegusa*

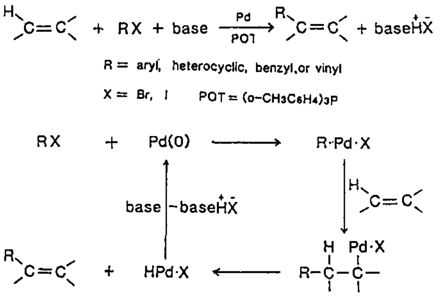
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, 606 Japan

Summary A group of polymers which have cinnamoyl skeletones in the main chain were synthesized using a coupling reaction between aryl halide moieties and acrylate (or acrylamide) moieties in the presence of a palladium catalyst. 2-(p-Iodobenzoxy)ethyl acrylate was polymerized to give a polymer having cinnamate skeletone. The polycondensation of 1,4-diiodobenzene with ethylene diacrylate produced a polyester having vinylene-phenylene-vinylene groups. Some other monomers were also studied for this novel polycondensation.

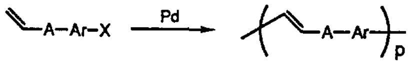
Introduction

Recently, many synthetic reactions which are catalyzed by palladium complexes have been explored because of its usefulness and uniqueness. Application of these reactions to polymer synthesis has been studied in our laboratory (1). This report deals with polymer synthesis using the coupling reaction between an aryl halide group and the C=C double bond of an acrylate (or acrylamide) derivative catalyzed by $Pd(OAc)_2$/tri-o-tolylphosphine(POT) system in the presence of an amine.

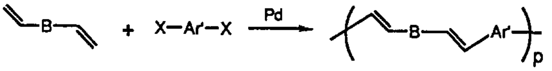
(Scheme 1)



The general scheme of a fundamental reaction of this polymerization, namely the Heck reaction, is shown as Scheme 1 (2). On the basis of this reaction, the following polymerizations can be designed (Eq.s 1 and 2).



Eq. 1



Eq. 2

HX is released in these polymerizations, which are classified as polycondensation. Concerning these types of polymerization including the coupling reaction not only on an alkenyl group but also on an alkynyl group, there have been several reports and patents which deal with syntheses of polyconjugated polymers possessing electro-conductivity or thermostability (3-7). However, the monomers in previous reports and patents are styrene or ethynylbenzene derivatives. Other olefinic monomers than styrene derivatives have not been investigated yet, so that we started our

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*To whom offprint requests should be sent work to extend the scope of this novel polymerization shown as Eq:s 1 and 2 (8). Very recently, Heiz and his co-workers also reported on systematical syntheses of monomers and polymers from styrene derivatives using the Heck reaction (9).

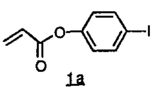
Experimental

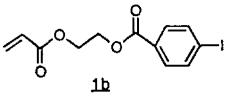
Materials Acrylic derivatives 1a, 1c, and 2a-2d were prepared by the reaction of acryloyl(or methacryloyl) chloride with the related alcohol (or amine), respectively. 1b was prepared by the reaction of 2-hydroxyethyl acrylate with p-iodobenzoyl chloride. 3b was prepared from p-iodophenol and α,ω-dibromo-3,6,9-trioxaundecane according to the modified method of the literature (10). p-Diiodobenzene and 4,4'-dibromobiphenylene were purified by recrystallization. Commercially available Pd(OAc)$_2$ and POT were used without purification. The solvents of DMF and pyridine were dried over CaH$_2$ and distilled.

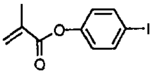
Polymerization A typical procedure was as follows. To the solution of p-diiodobenzene(456mg, 1.38mmol), Pd(OAc)$_2$(5.4mg, 0.024mmol), and POT (17.5mg, 0.058mmol) in DMF(4ml), were added triethylamine(567mg, 5.61mmol) and ethylene diacrylate(230mg, 1.35mmol). The mixture was heated at 60°C for 2hr under nitrogen atmosphere and, then, poured into methanol(80ml) to precipitate the polymeric product, which was collected by centrifugation. The obtained crude polymer was dissolved into o-chlorophenol(3ml). After the insoluble material was filtrated off, the solution was added into ether (80ml). The precipitated polymer was dried *in vacuo* (267mg, 81%). m-Cresol, CHCl$_3$/CF$_3$COOH(1v/1v), or DMF was also used as a good solvent in the reprecipitation of polymer.

Results and Discussion

Polymerization of acrylate derivatives having a p-iodophenyl group (a type of Eq. 1) Four acrylate derivatives 1a-1d were polymerized (Table 1). The polymer prepared from p-iodophenyl acrylate 1a was insoluble in any solvents other than H$_2$SO$_4$, which, however, degrated the product polymer. IR spectra of this polymer indicated the cinnamate (trans form) type structure (Fig. 1).


1a


1b


1c

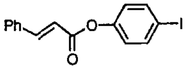

1d

Table 1. Polymerization of 1a-1d catalyzed by the Pd complex[a)]

No	Monomer	Temp.	Time	Yield[b)]	$\bar{M}n$ or [η]	m.p.	Color
1	1a	100°C	6 hr	108%			gray
2	1b	70	4.5	88	0.14[c)]	249°C	gray
3	1c	100	5	75	3100[d)]		yellow
4	1d	110	15	0			

a) Solvent, DMF; Pd(OAc)$_2$, 0.8-1.5mol%; POT, 1.6-3mol%; Et$_3$N(No 1, 3, and 4) or ^{n}Bu$_3$N(No 2), 2eq. for the monomer.

b) Calculated on the assumption that HX had been completely released.

c) m-Cresol, 30°C. d) GPC(PSt standard, CHCl$_3$).

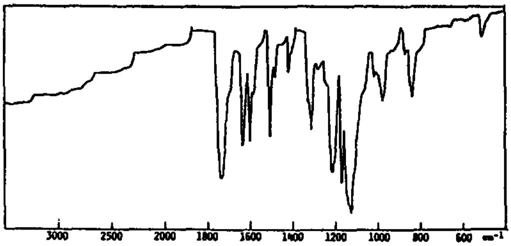


Fig. 1 IR spectra (KBr) of the polymer No 1.

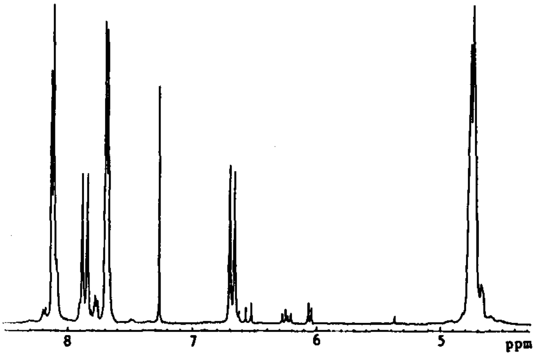
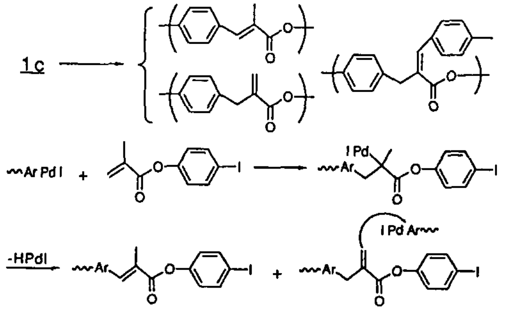


Fig. 2 Expanded ^1H NMR spectra (400 MHz) of the polymer No 2 in $CF_3CO_2D/CDCl_3$=1/1(v/v).

On the other hand, the polymer derived from 2-(p-iodobenzoxy)ethyl acrylate 1b was soluble in m-cresol and in trifluoroacetic acid, so that it was characterized in detail by ^1H NMR, which clarifies the structure (Fig. 2). Besides the bigger signals which indicate the main structure, some small signals are observed at δ6.05(d, J=10.5Hz), 6.24(dd, J=10.6 and 17.3Hz), 6.55(d, J=17.2Hz), 7.77(d, J=7.9Hz), and 8.19(d, J=8.2Hz). The former three signals are assignable to the olefinic protons of the acrylic group, which constitutes one terminal of the polymer. On the basis of the relative area of these signals to those due to the polymer main chain, $\overline{DP}$ was calculated at 21.4. On the other hand, the latter two signals are taken to indicate the other terminal of the polymer. The signal at δ7.77 indicates the existence of the unreacted iodophenyl group, and that at δ8.19 is probably due to four protons at 2,2'-position of a biphenyl group, which is produced by a side reaction, i.e., the coupling of two iodophenyl groups (c.f. the reaction of 1d).

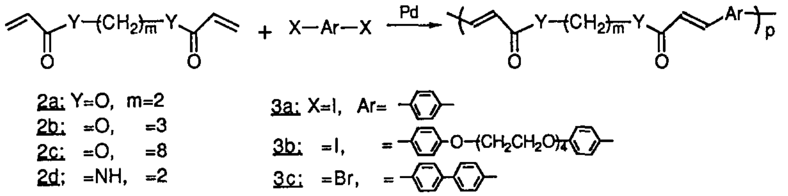
The polymers from 1a and 1b precipitated out with the progress of the reaction. On the other hand the reaction mixture from 1c was homogenous. The obtained polymer was soluble in a common solvent such as $CHCl_3$. The ^1H NMR spectra indicated that the polymer had three kinds of units(Scheme 2) since signals due to methylene protons between a phenylene group and a vinylene one were observed at δ3.78 and 4.10 along with a signal at δ7.90 due to a olefinic proton of α-methylcinnamate group. This is caused by the fact that there are two ways for β-hydrogen elimination in the intermediate (Scheme 2).

Scheme 2



When the monomer was α,β-disubstituted olefinic compound, i.e., p-iodophenyl cinnamate 1d, the polymerization did not occur. Only a biphenyl type compound, which was due to the coupling reaction of two iodophenyl groups, was obtained as a methanol insoluble portion.

Polymerization of bisacrylic derivatives with dihaloarene (a type of Eq: 2)



The above reaction successfully occurred to produce the polymer having the vinylene-phenylene-vinylene(all trans form) skeletons (Table 2). As an example, IR and ^{1}H NMR spectra of the polymer No 5 are shown in Fig. 3. In all runs except for No 6, the generated polymers gradually precipitated out as powders, which are insoluble in common solvent but soluble in p-chlorophenol, m-cresol, and trifluoroacetic acid.

The intrinsic viscosity of the resultant polymer from ethylene diacrylate 2a and p-diiodobenzene 3a had reached to a constant value at least after 2hr. Even in the homogenous system, i.e., the polymerization between 2a and tetraethylene glycol bis(p-iodophenyl) ether 3b, the growth of the polymer chain stopped within 4hr (Fig. 4).

Elemental analysis, i.e., the content of iodine is not so informative for the $\overline{\mathrm{DP}}$ of the polymer, since the coupling reaction between iodoarenyl groups, which occurs as mentioned in the preceding section, causes the incorrect estimation of the $\overline{\mathrm{DP}}$. For instance, iodine was not detected peculiarly in the polymer No 7.

When 4,4'-dibromobiphenyl 3c was used as a monomer in the place of the diiodo compound, the reaction was much slower and required higher reaction temperatures (No 9 and 10).

Table 2. Polymerization of 2 with 3 catalyzed by the Pd complex[a)]

No	Monomers[b)]	Temp.	Time	Yield[c)]	$\overline{M}n$ or $[\eta]$	m.p.	Color	Content of iodine[d)]
5	2a, 3a	60°C	2 hr	81%	0.17[e)]	260°C	yellow	5.04wt%
6	2a, 3b	60	4	78	17000[f)]		brown	1.88
7	2b, 3a	80	2.5	79	0.36[e)]	192	yellow	0
8	2c, 3a	75	2	84	0.35[g)]	190	yellow	0.74
9	2c, 3c	120	10	56	0.13[h)]		gray	
10[i)]	2c, 3c	120	24	95	0.22[h)]		gray	
11	2d, 3a	100	3	93	0.21[g)]		gray	1.79

a) Solvent, DMF(except for No 10); $Pd(OAc)_2$, 2mol%; POT, 4mol%; Et_3N(No 5-8 and 11) or $^nBu_3N$(No 9 and 10), 4eq. for 2.
b) Feed ratio of two monomers was 1:1.
c) Calculated on the assumption that HX had been completely released.
d) Elemental analysis.
e) p-Chlorophenol, 45°C.
f) GPC(PSt standard, $CHCl_3$).
g) m-Cresol, 30°C.
h) p-Chlorophenol/$CHCl_3$(5wt/1wt), 30°C.
i) Solvent, pyridine.

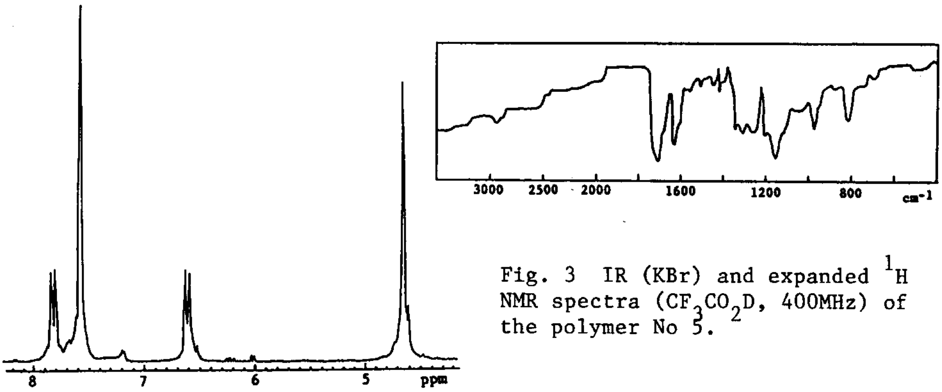


Fig. 3 IR (KBr) and expanded ^{1}H NMR spectra (CF_3CO_2D, 400MHz) of the polymer No 5.

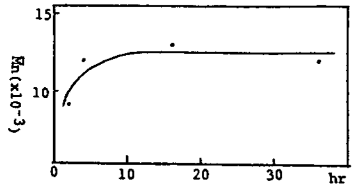


Fig. 4 A Time-Mn(GPC) curve in the polycondensation between 2 and 3b.

Polymerization of other olefinic monomers than acrylic derivatives

Whereas styrene derivatives such as divinylbenzene produced polymers (11), the reaction of an aliphatic diene such as 1,6-hexadiene with a dihaloarene resulted in cross-linking. The reaction of dimethyl fumarate, dimethyl maleate, or fumaronitrile with 4b hardly occurred resulting in a complex reaction.

Thermal character Some product polymers have crystallinity whose m.p. are shown in Table 1 or Table 2, respectively. In DSC measurement of all crystalline polymers, the first scan to 240-300°C showed an endothermic peak. However, no peak was observed on the cooling and the second heating scan. This is probably due to a cross-linking reaction between cinnamoyl skeletons in the polymer main chain, because the heating made the polymer insoluble in a solvent in which it was soluble before heated (12). DSC measurement of the polymer derived from 2c with 3c showed three(No9) or two(No10) endothermic peaks, which indicated the existence of mesophases (Fig. 5). Thermal stability of the polymer No 5 was investigated by TGA, which showed that the weight loss was rapid over 300°C (1% loss at 288°C).

Conclusion

The Heck reaction has successfully applied to polymer synthesis in the case of acrylate or styrene derivatives. However, steric hindrance disturbed the reaction, so that a polymer was not produced from a monomer with an α,β-disubstituted C=C double bond. Moreover, branching or cross-linking was caused by two directions of addition of an aryl palladium or by two ways of β-hydrogen elimination in the intermediate.

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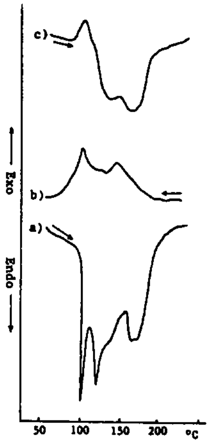

Fig. 5 DSC-curves of the polymer No 9;
a) the 1st heating scan,
b) the cooling scan, and
c) the 2nd heating scan.

Reference and Notes

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