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Notes

Polymerization of Some Fluorine-Containing Phenylacetylenes

HIROSHIGE MURAMATSU, TERUO UEDA, and KATSUKIYO ITO*

Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462, Japan.

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In the past, it had been difficult to prepare high molecular weight polymers from phenylacetylene.[1] Recently, Masuda et al.[2] have reported some methods to such synthesis. For instance, they reported the polymerization of 1-chloro-2-phenylacetylene (CPA) to $\bar{M}_w = 2 \times 10^6$, using a catalyst generated by UV irradiation of $Mo(CO)_6$.[2c]

In the present paper, we describe a method of polymerization[2] initiated by the catalyst formed by UV irradiation of $W(CO)_6$ which yields high molecular weight polymers from [*o*-(trifluoromethyl)phenyl]acetylene (*o*-TFMPA), [*m*-(trifluoromethyl)phenyl]acetylene (*m*-TFMPA), [*p*-(trifluoromethyl)phenyl]acetylene (*p*-TFMPA), and (*p*-fluorophenyl)acetylene (*p*-FPA). The polymerizabilities, polymerization yields, and molecular weights of the polymers are discussed, and the rigidity of the polymer chain of poly (*o*-TFMPA) is compared with that of poly(CPA).

Experimental Section

o-TFMPA was prepared by a method as described before.[4] *m*-TFMPA, *p*-TFMPA, and *p*-FPA were provided by Dr. Okuhara in this Institute and poly(CPA) was supplied by Sanyo Chemical Industries, Ltd. A solution (25 cm[3]) of $W(CO)_6$ in carbon tetrachloride was irradiated with UV light of a 100-W high-pressure mercury lamp (Ushio Electric Inc.) at 40 °C for 30 min, monomer was added to this solution, and polymerization was run in the dark at 40 °C for 24 h.[2] The polymerization was terminated with methanol, and the precipitated polymers were purified by dissolving into tetrahydrofuran and reprecipitating with methanol, filtered off, washed with methanol, and dried to a constant weight.

Intrinsic viscosities were measured in tetrahydrofuran (THF) at 38 °C and in toluene at 30 °C. Weight-average molecular weights were determined in THF with an LS-8 low-angle laser light scattering photometer (Toyo Soda Manufacturing Co., Ltd). The values of K and a in the Mark–Houwink equation, $[\eta] = KM^a$, were estimated by using the equation[3]

$$\frac{[\eta]\bar{M}_w}{K_s} = [\sum_{j=1}^{\infty} w_j M_{js}^{a(1+a_s)/(1+a)}][\sum_{j=1}^{\infty} w_j M_{js}^{(1+a_s)/(1+a)}] \quad (1)$$

where $[\eta]$ is intrinsic viscosity, M is molecular weight, K_s and a_s are Mark–Houwink constants for polystyrene, w_j is the weight fraction of the jth species of the polymer in the measurement of the gel permeation chromatogram (GPC), and M_{js} is the molecular weight of the jth species of polystyrene. An HLC-802A GPC (Toyo Soda Manufacturing Co., Ltd) was used in the present work.

Results and Discussion

The data on the polymerizations are shown in Table I. The color of all the polymers was darker red than poly(phenylacetylene) (PA) and quite different from that of poly(CPA), which is light yellow.[1,2] All the polymers had absorptions in the range 1570–1670 cm^{-1} for conjugated double bonds.[1,2]

Polymerization with $[W(CO)_6] = 60$ mmol/L gave generally good yields except for poly(*p*-TFMPA). The polymers had molecular weights greater than 10^4, those of poly(*o*-TFMPA) and poly(*m*-TFMPA) were larger than that of PA,[2] and that of poly(*p*-TFMPA) was comparable to that of PA. The molecular weight of poly(*p*-FPA) was less than that of PA. From the results, the polymerizability decreases in the order *o*-TFMPA > *m*-TFMPA > *p*-TFMPA. This suggests that the polymerizability is affected by the electronegativity of the CF_3 group, which decreases with increasing distance between $C{\equiv}H$ and CF_3, regardless of the steric hindrance of CF_3.[5]

Table I
Data on the Polymerization of Fluorine-Containing Phenylacetylenes

monomer	[M], mol/L	$[W(CO)_6]$, mmol/L	yield, %	$\nu_{\text{-C=C-}}$[a]	$\bar{M}_w/10^4$
o-TFMPA	1.27	60	100	1590, 1618	26.1
o-TFMPA	0.76	60	100		13.3
o-TFMPA	0.38	60	100		12.2
o-TFMPA	0.19	60	100		9.2
o-TFMPA	1.27	10	90		159
m-TFMPA	1.22	60	78	1570, 1670 (br, weak)	15.4
p-TFMPA	1.08	60	41	1602, 1618	2.8
p-FPA	1.59	60	97	1610	1.1

[a] IR absorption for conjugated double bonds in polymer.

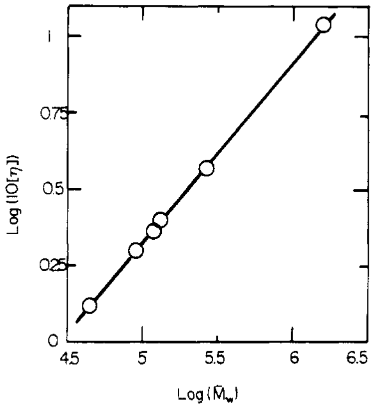

Figure 1. Relationship between intrinsic viscosity and weight-average molecular weight for poly(*o*-TFMPA) in toluene at 30 °C.

In the polymerization of *o*-TFMPA when $[W(CO)_6] > 10$ mmol/L, we obtained a quantitative yield of poly(*o*-TFMPA), but the yield decreased rapidly with decreasing catalyst concentration for $[W(CO)_6] \leq 10$ mmol/L. The polymer molecular weight increased with decreasing monomer concentration. Such an increase was observed in the polymerization of CPA. As expected, the polymer molecular weight increased with decreasing catalyst concentration. This is rather different from the result obtained in the polymerization of CPA, where the molecular weight of poly(CPA) is relatively insensitive to catalyst concentration.

A relationship between intrinsic viscosity and weight-average molecular weight for poly(*o*-TFMPA) in toluene at 30 °C is shown in Figure 1. This logarithmic plot gives a straight line as required by the Mark–Houwink equation with $K = 2.1 \times 10^{-4}$ dL/g and $a = 0.60$. The exponent a is significantly different from $a = 1.07$ of poly(CPA).[2c] The following equations in THF at 38 °C were also obtained.

$$[\eta] = 2.7 \times 10^{-5} M^{0.59} \quad \text{for poly}(o\text{-TFMPA}) \quad (2a)$$

$$[\eta] = 5.5 \times 10^{-6} M^{0.85} \quad \text{for poly(CPA)} \quad (2b)$$

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From these results, it is apparent that the exponent *a* for poly(*o*-TFMPA) is smaller than that for poly(CPA), which implies that the polymer chain of poly(*o*-TFMPA) is less rigid than that of poly(CPA).

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Registry No. $W(CO)_6$, 14040-11-0; *o*-TFMPA (homopolymer), 96504-22-2; *p*-TFMPA (homopolymer), 96504-19-7; *p*-FPA (homopolymer), 96504-20-0; *m*-TFMPA (homopolymer), 96504-21-1.

References and Notes

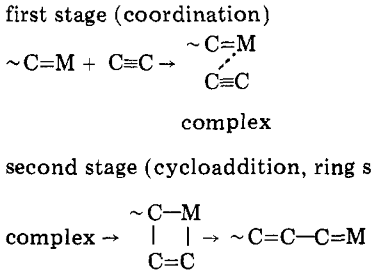
(1) R. J. Kern, *J. Polym. Sci., Part A-1*, **7**, 621 (1969); T. Higashimura, Y.-X. Deng, and T. Masuda, *Macromolecules*, **15**, 234 (1982). See also papers cited in these references.

(2) (a) T. Masuda, Y. Kuwane, K. Yamamoto, and T. Higashimura, *Polym. Bull.*, **2**, 823 (1980); (b) T. Masuda, Y. Okano, Y. Kuwane, and T. Higashimura, *Polym. J.*, **12**, 907 (1980); (c) T. Masuda, Y. Kuwane, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1043 (1982); (d) T. Masuda, T. Yoshizawa, Y. Okano, and T. Higashmura, *Polymer*, **25**, 503 (1984). See also papers cited in these references.

(3) H. K. Mahabadi and K. F. O'Driscoll, *J. Appl. Polym. Sci.*, **21**, 1283 (1977).

(4) K. Kodaira and K. Okuhara, Japanese Patent Application 1982-033329; Meeting of the Chemical Society of Japan, Tokyo, Apr 1982, No. II, p 1081.

(5) In the W-catalyzed polymerization of substituted acetylenes, the propagation reaction is inferred to proceed via metal carbenes [T. J. Katz and S. J. Lee, *J. Am. Chem. Soc.*, **102**, 422 (1980)]. Masuda et al.[2d] suggested the following mechanism.



They stated that the coordination ability of the acetylenic monomers is governed mainly by the steric factor. Since our results show the effect of the electronegativity of the CF_3 group in monomers on the polymerizability, the propagation seems to be controlled at the second stage in the present polymerizations.

Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 5. Comparison with Three Alternative Models

JEFFREY SKOLNICK*,† and ROBERT YARIS

Department of Chemistry, Washington University, St. Louis, Missouri 63130. *Received October 19, 1984*

Over the past several years, to examine local relaxation processes in polymers we have developed a damped orientational diffusion model[1-4] of polymer local main-chain motion. In this model[1] the main-chain orientational motion is treated in the context of a continuum damped diffusion equation where the discrete nature of local polymer motion is recognized by introducing a short-wavelength cutoff that corresponds (roughly) to the smallest motional unit and where the interaction of the diffusing mode with the solvent is modeled by a damping constant. The resulting damped diffusion model (DD) can be analytically solved for the normalized orientational autocorrelation function

$$\Phi_{DD}(t) = \tfrac{1}{2}e^{-\beta t}(\pi/\delta t)^{1/2}\,\mathrm{erf}\,[(\delta t)^{1/2}] \qquad (1)$$

$\Phi_{DD}(t)$ depends on two adjustable parameters: β, the damping constant, and δ, an effective small-scale jump rate ($=Dk_m^2$, where D is the diffusion constant or jump probability, and k_m is the wave vector cutoff corresponding to the minimum allowed motional unit). More recently, we have extended this model to include the effects of chain–chain interactions by using a complex damping constant[3] and to include the effect of side chains on local main-chain motions.[4] For a regular repeating array of side chains, it has been shown that side chains merely modify the main-chain damping constant. We have demonstrated[2] that NMR and local dielectric relaxation processes can be adequately described by this model.

Recently, Viovy, Monnerie, and Brochon presented a very detailed study of the fluorescence depolarization of polystyrene in dilute solution and showed that the damped diffusion model fits their measured autocorrelation function very well and that the parameters of the model were insensitive to the size of the fitting window about zero time.[5] Actually, they used an earlier version of the model[6] which employed a hard rather than a soft long-wavelength cutoff to represent the effect of the damping. However we have shown[2] that the two versions of the model lead numerically to the same correlation function. Since the physical interpretation of the damping is more apparent with the soft rather than with the hard cutoff, we shall refer to the latter damped diffusion version of the model.

Another model that has been used to fit local relaxation processes in polymers is the Hall–Helfand model[7] (HH). In this model, two processes are considered, an individual reorientation process which leads to an exponential decay, and a cooperative process where the correlation diffuses down the chain. This leads to an autocorrelation function of the form

$$\Phi_{HH}(t) = e^{-\kappa_0 t}e^{-\kappa_1 t}I_0(\kappa_1 t) \qquad (2)$$

where I_0 is a modified Bessel function. Here κ_0 corresponds to the individual reorientation relaxation constant and the terms containing κ_1 correspond to the cooperative motion.

Recently, Weber and Helfand[8] calculated orientational autocorrelation functions using a Brownian dynamics simulation and were not able to fit the calculated orientational correlation function with the Hall–Helfand functional form. They argued that there are also slower decaying processes and hence used a modified Hall–Helfand (MHH) correlation function

$$\Phi_{MHH}(t) = (1-\alpha)\Phi_{HH}(t) + \alpha e^{-\mu t} \qquad (3)$$

where μ is a decay constant modeling the slow decay processes and α is a mixing coefficient. The modified Hall–Helfand correlation function contains four parameters and fits the computer simulation very well.

Following the assumption of Weber and Helfand,[8] if in addition to the local reorientation processes embodied in $\Phi_{DD}(t)$, the autocorrelation function of interest is sensitive to long-wavelength, slowly decaying modes, it is natural to consider the modified damped diffusion autocorrelation function (MDD)

$$\Phi_{MDD}(t) = (1-f)\Phi_{DD}(t) + fe^{-\xi t} \qquad (4)$$

Here f and ξ are the DD analogues of α and μ. In both the MHH and MDD cases the long-wavelength parameters by definition must be insensitive to local details and are thus "hydrodynamic" in nature.

[†] Alfred P. Sloan Foundation Fellow.

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