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Laser-initiated homogeneously photocatalytic polymerization of phenylacetylene by $W(CO)_6$-CH_3I system

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Summary

The polymerization of phenylacetylene at room temperature by UV laser activated $W(CO)_6$ in CH_3I solvent was investigated. The weight-average molecular weight of the polymer is 10^3, and the ^1H NMR spectra of polymers indicate that the polyphenylacetylene has a cis-transoidal structure. The experimental data show that not only laser wavelength, energy and irradiation time influence on the yield of polymer but also the laser energy influences the structure of polymer.

Introduction

Metal carbonyl complexes are well known to undergo light induced loss of CO in solution to give coordinatively unsaturated organometallic species which are catalysts[1]. Among the wide array of metal carbonyl complexes, It is proved that $W(CO)_6$- CCl_4 is a typical catalyst system for the polymerizations of cycloolefins and akynes, the isomerizations of olefins, and the metatheses of olefins under mild condition[2–7].

The photocatalytic polymerizations of phenylacetylene(PA) by light activated $W(CO)_6$-CCl_4 have been studied. However, all experiments have accompanied with low quantum yield and long irradiation time. In 1990, K.J.Fu et al[8] have developed the laser induced photocatalytic polymerization of phenylacetylene using $W(CO)_6$-CCl_4 catalyst system and the trans- cisoidal polyphenylacetylene(PPA) was obtained. The adjustable wavelength and high energy density increase the quantum yield and the yield of polymer, and short the irradiation time.

In the present study, UV laser(532, 355 and 266nm) has been used to polymerize the phenylacetylene by $W(CO)_6$-CH_3I catalyst system. The dependences of yield and character of polymer on laser parameters were investigated. Experiment results show that unlike the $W(CO)_6$-CCl_4, the $W(CO)_6$-CH_3I catalyst system leads to formation of homogeneous catalyst, low molecular weight of polymer, cis- transoidal structure of polymer, and control of cis- content of polymer.

Experimental

UV pulsed laser is frequency doubled, tripled, and quadrupled Nd^{3+}: YAG pulsed laser (Quanta-Ray) operating at 532, 355 and 266nm respectively. The pulse duration is 6ns and repetition rate 10Hz. The output of laser was monitored with a energy meter.

Phenylacetylene(Fluka AG, purity>97%) was dried over with CaH_2 ,and distilled twice at reduced pressure. $W(CO)_6$(Aldrich Chemical Inc) used without further purification. CH_3I was dried over with CaH_2 and distilled twice.

Our experimental process was as follows: The laser beam was directed into the CH_3I solution(6ml) of $W(CO)_6$(16mM) while the solution was continuously stirred with a magnetic stirrer. After being irradiated for a period of time, the homogeneous catalyst

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was formed and immediately added to phenylacetylene. The mixture was kept in dark at room temperature for 24 hours, and the color of solution was changed from green yellow to red. Both the irradiation and polymerization procedure were carried out under a dry argon atmosphere. The polymer was obtained by adding CH_3OH, filtering the precipitate, and drying to a constant weight.
The yield of polymer was determined by dividing the weight of polymer by the weight of monomer. The weight-average molecular weight (MW) of polymer was determined by light scattering method. The structure of polymer was characterized with ^1H NMR spectrometer(Uarine-Unity 200).

Results and Discussion

The effects of laser parameters on polymer yield
Experiment data show that no polymer was obtained under the irradiation with 532 and 266nm or without UV irradiation. This is because that $W(CO)_6$ has no absorption in visible region, and CH_3I has a stronger absorption at 266nm than $W(CO)_6$. Thus only 355nm is efficient for the photolysis of $W(CO)_6$. When the monomer and catalyst solution were irradiated together, the yield of polymer was low. This is maybe due to the partial absorption of UV light by the monomer. The yield and molecular weight of polymer obtained at different laser energy and irradiation time, as shown in table 1, show that the yield of polymer becomes higher with the increase of laser energy and irradiation time, but the MW values of polymer obtained at different laser energy and irradiation time are nearly 10^3.

Table 1. Effects of laser energy and irradiation time on yield and molecular weight of polymer

$M_o(CO)_6$ (mM)	Laser Parameters			Yield (%)	MW (10^3)
	wavelength (nm)	Energy (mJ/P)	Irradiation time (min)		
16	355	4	30	18	5.58
16	355	6	30	22	5.88
16	355	10	30	40	5.15
16	355	10	5	10	4.68
16	355	10	15	20	——
16	355	10	50	80	4.25

The effect of laser energy on the cis-content of polymer

The experimental data show that the laser energy has an obvious effect on the cis-content of polymer. The ^{1}H NMR spectra of polymers obtained at different laser energy are shown in figure 1.

We have known that the ^{1}H NMR spectrum of cis-transoidal structure of polyphenylacetylene has three resonances centered at σ=5.82ppm (one cis polyenic proton), σ=6.7 ppm (one aromatic proton) and σ=6.85 ppm, and the cis-content in cis-transoidal polyphenylacetylene was determined from ^{1}H NMR spectrum, using the area of the peaks from σ=5.82($A_{5.82}$) to the total area of spectrum(A_t) according to Eq.(1)

$$\%cis = \frac{A_{5.82} \times 10000}{A_t \times 16.66} \tag{1}$$

For figure 1a, the cis-content is 76%, and for figure 3b-d, the cis content(<70%) can not be determined from the ^{1}H NMR spectrum, due to the superosition of σ=5.82 signal with the resonance of aromatic protons. This indicates that the cis-content of polymer can be controlled by adjusting the laser energy. This is probably because that the excess of catalytic center formed by the increase of laser energy leads to the transformation of cis-transoidal of polymer to trans- cisoidal.

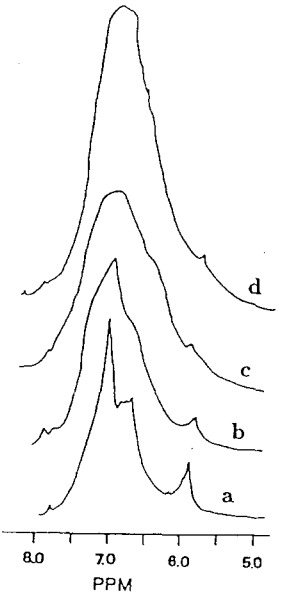

Figure 1. Curve a-d, the typical ^{1}H NMR spectra of cis-transoidal polymers obtained with different incident laser energy 2,4,6, and 10mJ/p. Laser irradiation time 30 minutes and polymerization time 24 hours. [W(CO)$_6$]=16mM and [PA]=2.3M.

The effect of polymerization time on polymer yield

The polymerization of phenylacetylene indicates that the laser is only necessary to produce the homogeneous catalyst, and the polymerization of monomer spontaneously carries out under the catalyst. The yields of polymers obtained as the function of polymerization time are shown in figure 2.

Figure 2 shows that the yield of polymer exponentially increases with polymerization time.

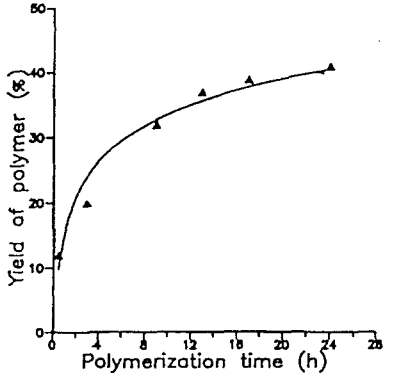

Figure 2. Dependence of yield of PA on polymerization time. Laser energy is 10 mJ/p and laser irradiation time 30 minutes.[$W(CO)_6$] =16mM and [PA] =2.3M.

Comparison between $W(CO)_6$-CCl_4 and $W(CO)_6$- CH_3I catalyst system

Figure 3 shows the typical ^1H NMR spectrum of cis-transoidal polyphenylacetylene obtained by $W(CO)_6$-CCl_4 catalyst system.

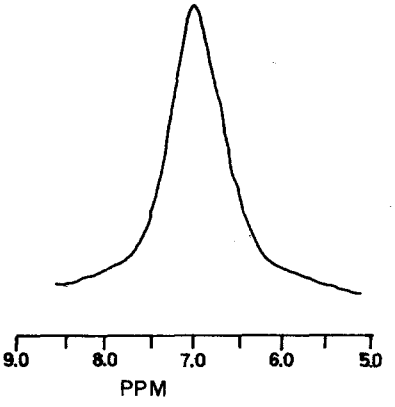

Figure 3. The typical ^1H NMR spectra of trans- cisoidal polymers. Laser energy 40mJ/p, laser irradiation time 30 minutes and polymerization time 24 hours. [$W(CO)_6$]=16mM and [PA]=2.3M.

Table 2 shows the yield, structure and molecular weight of polymer obtained by $W(CO)_6$-CCl_4[8] and $W(CO)_6$-CH_3I respectively . Both $W(CO)_6$-CCl_4 and $W(CO)_6$-CH_3I are efficient for the polymerization of phenylacetylene, but the structure and MW values of polymers obtained by them are different.

Table 2. Comparison between $W(CO)_6$-CCl_4 and $W(CO)_6$-CH_3I in the polymerization of phenylacetylene

Catalyst system	Catalyst	Yield (%)	Structure	MW
$W(CO)_6$-CH_3I	Homogeneous	40	Cis-transoidal	5150
$W(CO)_6$-CCl_4	Hetergeneous	44	Trans-cisoidal	37000

Conclusion

A study of laser photocatalytic polymerization of phenylacetylene by $W(CO)_6$-CH_3I shows that homogeneous catalyst is efficient. Not only the laser energy and irradiation time obviously influence the yield of polymer but also laser energy obviously influences the structure of polymer. Moreover by using $W(CO)_6$-CH_3I and $W(CO)_6$-CCl_4 catalyst system, we have realized the stereoselective polymerization of phenylacetylene.

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