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Laser photocatalytic polymerization of phenylacetylene

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Summary

The polymerization of phenylacetylene induced by ultraviolet laser (266 and 355 nm) irradiation of $W(CO)_6$ and $W(CO)_6$-$TiCl_4$ in CCl_4 solvent was investigated. The weight-average molecular weights of the polymers reach 10^5. The infrared spectra indicate that the polymers have a trans-rich conjugated double bond structure. The influence of laser energy, laser wavelength and irradiation time on the polymerization was examined. Experimental data show that laser energy and wavelength are the most effective factors.

Introduction

Metal carbonyl complexes are well known to undergo light induced loss of CO ligand in solution to give coordinatively unsaturated organometallic species which are potent catalysts. It was proved highly efficient for laser initiated hydrogenation, isomerization and hydrosilation in mild condition. Recently K. J. Fu et al have developed analogous laser-initiated photocatalytic polymerization using metal carbonyl and found that laser energy, wavelength, repetition rate and irradiation time have influenced the polymerization(1). Other types of laser initiated polymerization of charge-transfer monomers and vinyl monomers have also attracted a great attention

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*To whom correspondence should be addressed in recent years(2-6). In contrast to conventional light sources, laser can excite catalytic precursors specifically without dispersing energy. In addition, pulsed laser technique can be used in transient spectroscopy to monitor time-resolved reaction processes, which is very useful for understanding photocatalytic dynamic processes.

Polymerization of phenylacetylene has been studied under different conditions, such as radical initiation, cationic and coordinative mechanisms(7-16). However, most experiments have often accompanied with low molecular weight. Masuda et al firstly found that transition metal complexes were effective initiators to obtain polyphenylacetylene in a high yield(7-12). Last year Ehrlich et al reported Xenon arc gas discharge lamp photocatalytic polymerization of phenylacetylene in $W(CO)_6$-CCl_4 system, they obtained additional information on reaction mechanism(16).

In the present study UV laser (355 and 266 nm) has been used to polymerize phenylacetylene in both $W(CO)_6$-CCl_4 and $W(CO)_6$-$TiCl_4$-CCl_4 systems. We have investigated the dependence of polymer yield and character on laser parameters. Experiments showed that the irradiation of $W(CO)_6$-$TiCl_4$-CCl_4 catalyst system led to higher monomer conversion polymers than those provided by $W(CO)_6$-CCl_4 system.

Experimental

The laser used was double, triple and quadruple frequency of Nd^{3+}:YAG pulsed laser (Quanta-Ray) operating at 532, 355 and 266nm, pulse duration 6ns and repetition rate 10Hz. The output of laser was detected by an energy meter.

Phenylacetylene (Fluka AG, purity$\rangle$97%) was dried over calcium hydride or 5A molecular sieves and finally distilled twice at reduced pressure. $W(CO)_6$ (Aldrich Chemical Company, Inc.) and $TiCl_4$ (Beijing Chemical Company, A.R.) were used without further purification. CCl_4 solvent (Beijing Chemical Company, G.R.) was dried over 5A molecular sieves before experiment.

In our experiment two catalyst systems were used: 1. a solution (5ml) of $W(CO)_6$ (0.10mmol) in CCl_4, 2. a solution (5ml) containing $W(CO)_6$ (0.10mmol) and $TiCl_4$ (0.10mmol) in CCl_4. The laser beam was directed into the catalyst solution with reflecting mirrors while the solution was continuously stirred with a magnetic stirrer. After being irradiated for a period of time which depended on different experiments (usually from 10 to 60 minutes), the catalyst solution was immediately poured into 5ml solution of phenylacetylene(10mmol) in CCl_4. The mixture was kept in dark at room temperature for 24 hours. All the irradiation and polymerization procedures were carried out under a dry argon atmosphere. The polymers formed were precipitated in methanol, filtered off, washed with methanol several times, and dried to constant weight.

The polymer yields were determined by gravimetry. Monomer conversion was calculated by dividing the polymer weight by the weight of the monomer. Weight-average molecular weights Mw were determined by light scattering method from Zimm plot using Photal DLS-700 spectrophotometer. Elemental analyses were performed by using a MOD 1106-CARLO ERBA elemental analyzer. IR spectra of polymers were recorded on a NICOLET 60SXB IR spectrometer.

Results and Discussion

The polymers yielded are dark red to orange powders depending on different experimental conditions. The results of element analyses of polymers agree with the composition calculated for $(C_8H_6)_n$. The infrared spectra indicate that the polymers are rich in trans-structure. In the following we will discuss the polymerization with the two catalyst systems under different conditions.

The effect of laser wavelength on polymerization

Experiments showed that no polymer was obtained under irradiation at 532nm or without UV irradiation. This is because $W(CO)_6$ and $TiCl_4$ have maximum absorption in UV region and have no absorption in visible region. When the monomer and catalyst were irradiated together in solution, the monomer conversion was low. This may be due to the partial absorption of UV light by the monomer. The table lists the effect of laser wavelength on polymerization. The results show that the polymers obtained by irradiation at 266nm light have higher molecular weights than those obtained by irradiation at 355nm, and the monomer conversion gets higher when pulse energy reaches 10mJ. This is slightly different from the work of Masuda et al(11) in which they demonstrated that UV light at 334 - 365nm was useful in producing active species for polymerization. It can also be concluded from the table that the conversion for $W(CO)_6$-$TiCl_4$-CCl_4 catalyst system is higher, so this system has higher catalytic activity than $W(CO)_6$-CCl_4 system.

Table The effect of laser wavelength on the polymerization

$W(CO)_6$ (mM)	$TiCl_4$ (mM)	Wavelength (nm)	Energy (mJ/p)	Conversion (%)	Mw (10^5)
10	0	355	4	34	0.26
10	0	266	4	4	
10	10	355	4	85	0.42
10	10	266	4	33	1.01
10	0	355	10	44	0.37
10	0	266	10	48	2.04
10	10	355	10	84	0.68
10	10	266	10	83	0.60

The effect of laser energy on polymerization

Figure 1 shows the dependence of monomer conversion on laser energy at the same irradiation time (10 minutes). The monomer conversion becomes higher with the increase of laser energy and is quantitative 97% at high energy just in 10 minutes. The weight-average molecular weights of polymers obtained at different laser energy are 10^4 - 10^5.

The effect of irradiation time on polymerization

The experiments showed that irradiation time had no obvious influence on the average molecular weights of polymers. Figure 2 illustrates the dependence of monomer conversion on irradiation time for the two catalyst systems. The results show that the monomer conversion increases gradually with increasing irradiation time. Nevertheless, the influence of irradiation time on the polymerization is not so obvious as

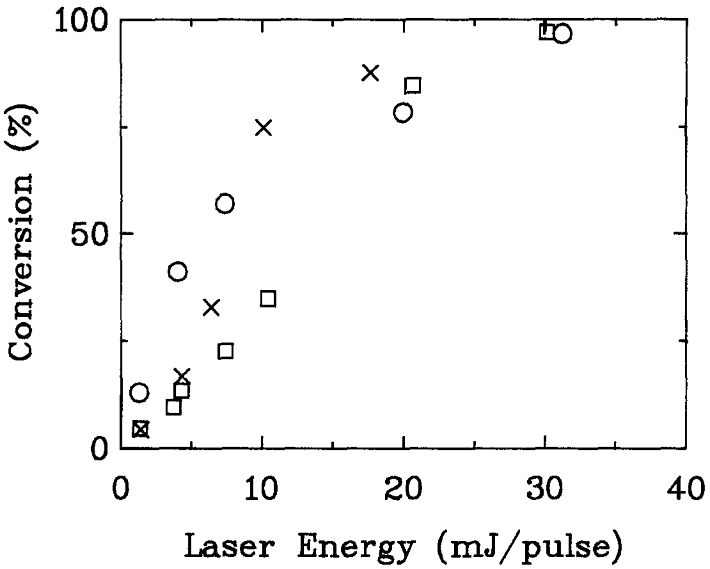

Fig. 1. Dependence of monomer conversion on laser energy. Irradiation time 10 minutes, $[C_8H_6]$=1M, $[W(CO)_6]$=10mM, $[TiCl_4]$=10mM. (O) $W(CO)_6$-$TiCl_4$-CCl_4 system, 355nm, (□) $W(CO)_6$-CCl_4 system, 355nm, (×) $W(CO)_6$-$TiCl_4$-CCl_4 system, 266nm.

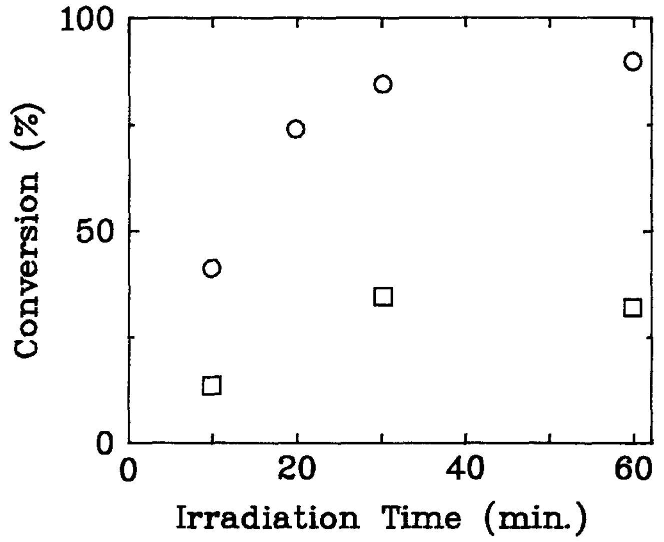

Fig. 2. Dependence of monomer conversion on irradiation time. Laser energy 4mJ/pulse, wavelength 355 nm, $[C_8H_6]$=1 M, $[W(CO)_6]$=10 mM, $[TiCl_4]$=10 mM. (O) $W(CO)_6$-$TiCl_4$-CCl_4 system, (□) $W(CO)_6$-CCl_4 system.

that of laser energy. Extending irradiation time do not achieve very high polymer yield especially for $W(CO)_6$-CCl_4 system.

Conclusions

A study of laser photocatalytic polymerization of phenylacetylene with two catalyst systems shows that laser operating parameters have influence on the polymerization. High laser energy can lead to polymers with high monomer conversion. The new catalyst $W(CO)_6$-$TiCl_4$-CCl_4-UV has higher catalytic activity than $W(CO)_6$-CCl_4-UV, this result is similar to Nagasawa et al's result in olefin metathesis catalysts using mercury lamp(17). Association of the coordinatively unsaturated $W(CO)_5$ and $TiCl_4$ was suggested to be a key step in the formation of a catalytically active complex(17). Further study about mechanism is in progress.

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