

Influence of Montmorillonite on Syndiotactic Polymerization Behavior of Styrene

Feng Yang,¹ Xuequan Zhang,² Haichao Zhao,² Weimin Dong,² Baotong Huang²

¹Department of Material Science and Engineering, Shen Yang Institute of Chemical Technology, Shenyang 110142, People's Republic of China

²Polymer Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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ABSTRACT: The influence of montmorillonite (MMT) on the syndiotactic polymerization behavior of styrene was studied. To avoid the hydrophilic surface of the MMT coming into contact with the catalyst, which could poison it, SAN was introduced between the MMT and Cp*Ti(OCH₃)₃. MMT was introduced into the catalytic system as a supporter for the Ti catalyst (supported catalytic system) or just dispersed in the polymerization solvent directly (*in situ* polymerization system). The polymerization results showed that surface modification of MMT dramatically

affected the catalytic activity as well as the syndiotacticity of the polymers. This is mainly explained by the insulator SAN preventing the formation of the inactive/little active species Si—O—Ti and other atactic active species resulting from the reaction of the —OH on the MMT layer surface with Cp*Ti(OCH₃)₃. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2755–2759, 2007

Key words: catalysts; syndiotactic polystyrene; montmorillonite

INTRODUCTION

Since catalysts for the syndiospecific polymerization of styrene were discovered,¹ there has been great interest in them because of the excellent properties of syndiotactic polystyrene (sPS). The initial interest was mainly in the catalytic systems, such as the nature of the catalyst, the cocatalyst, and the other minor components. A variety of syndiospecific catalytic systems has been reported, such as compounds (TiX₄, where X = Cl, OR, R) and “half-metallocene” compounds (CpMX₃, where M = Ti, Zr, Hf).² With the appearance of problems of reactor fouling and control of morphology, much effort was focusing on adapting these homogeneous catalytic systems to the requirements of practical applications. Supporting the active species on a solid is always expected to be an efficient solution. Inorganic compounds such as SiO₂,^{3–7} Al₂O₃,^{6,8} and magnesium compounds,^{9,10} as well as organic polymers,^{11,12} have been used as carriers for supported catalysts. Soga and Nakatani³ and Pasquet and Spitz¹³ found that SiO₂-supported catalysts performed well (relatively high activity and high syndiotacticity) in styrene polymerization.

Montmorillonite, a 2 : 1 layered silicate whose lamellae are constructed of two tetrahedral silicate sheets

sandwiching one octahedral sheet, readily accepts the intercalation of compounds into the interlayer spaces, where a variety of guest species can be inserted in such a way that the host layer remains essentially undistorted. Robust, widely spaced polyatomic guest ions push the host layers apart, leaving large areas of empty intragallery space available for catalytic activity. The high layer rigidity of MMT also makes it possible to delaminate clays into single sheets 1 nm thick by 1 μm in lateral dimension.¹⁴ As a result of its high layer rigidity and structural anisotropy, MMT exhibits diverse properties that have found a wide variety of applications including in chemical catalysis and polymer nanocomposites.¹⁵

Moreover, MMT possesses characteristics that make it a suitable carrier for a styrene polymerization catalyst, such as a chemical surface similar to that of silica and a big surface area, as well as mechanical stability and thermal stability. The unique advantage of MMT as a carrier is that, on the one hand, it serves as support, resolving the problems of reactor fouling and control of morphology, and on the other hand, as a result of its large aspect ratio and nanostructure, it also can function as a nanofiller that enhances the mechanical and thermal properties of sPS.

So far there have been few studies of the effect of MMT on the syndiotactic polymerization behavior of styrene. Shen et al.¹⁶ reported sPS/montmorillonite nanocomposites prepared by the intercalation of the organometallic catalyst and monomer into MMT and

Correspondence to: Feng Yang (yf18231@yahoo.com.cn).

then polymerization *in situ*. They mainly focused on the structure and properties of the nanocomposite obtained.

The key to introducing MMT into a styrene polymerization system is that the catalyst species can be supported on the MMT efficiently without sacrificing the high activity and high syndiotacticity of the homogeneous catalyst. To protect the active species from the influence of the poisonous hydrophilic surface of the MMT, a polymer that is completely absorbed or anchored on the surface of the MMT to serve as a medium or an insulation material between MMT and catalyst is a necessary component. The requirements for this polymer are: (1) being harmless to catalyst performance, (2) chemically or physically interacting with the catalyst and the support, and (3) being insoluble in styrene monomer and polymerization solvent. Polymers that meet these requirements are those containing specified polar groups, such as acrylonitrile-containing polymers and copolymers and hydroxyl group-containing polymers and copolymers.

Stimulated by recent advances in polymer/MMT composite preparation and based on our experience with supported catalysts in styrene, we developed a novel supported catalyst, Ti/SAN/MMT, with SAN anchored on the surface of MMT, and Ti attached on the surface of MMT through the SAN. To explore the influence of montmorillonite on the syndiotactic polymerization of styrene, the homogeneous catalytic behavior and *in situ* polymerization system, that is, MMT, did not serve as a catalyst carrier; instead, it was just dispersed in the polymerization solvent of the homogeneous catalytic system directly, and then polymerization *in situ* also was studied. Mainly, the effects of SAN on the catalytic properties were investigated.

EXPERIMENTAL

Materials

$\text{Cp}^*\text{Ti}(\text{OCH}_3)_3$ was kindly supplied by Strem Co. (Odessa State, Ukraine) and diluted with toluene to make a 1×10^{-6} M solution. Montmorillonite (Kunipia F) was supplied by the Kunimine Co. (Japan). This clay mineral bears exchangeable sodium ions with an exchange capacity of 119 meq/100 g. Styrene and acrylonitrile were purchased from Tianjing Reagent Factory and purified by distillation under reduced pressure. Potassium persulfate, as free-radical initiator, magnesium sulfate, as coagulant, and sodium dodecyl sulfonate, as emulsifier, were used as received. Toluene was refluxed over sodium/benzophenone ketyl and distilled before use. Methyaluminoxane (MAO) in toluene (10 wt %) was purchased from the Ethyl Corp. Triisobutylaluminum (TIBA) was purchased from Aldrich and diluted with toluene to make a 1M solution.

Preparation of SAN-modified MMT

SAN-modified MMT (SAN/MMT) was prepared by emulsion polymerization. First, 0.5 g of sodium dodecyl sulfonate was added to 1000 mL of MMT slurry (1 wt %) in distilled water at room temperature. After stirring for 3 h and sonicating for 1 h, the mixture was heated to 70°C. Then 8 mL of styrene and 2 mL of acrylonitrile were added. Polymerization was started when a 1 wt % potassium sulfate solution was dripped into the flask. The mixture was kept standing for 3 h before the emulsion colloid was poured into distilled water containing 10% magnesium sulfate. After further stirring for 30 min, the white precipitated hybrid was centrifuged, further washed with distilled water 3 times, and dried under reduced pressure at 40°C for 24 h before being extracted with boiling toluene.

Preparation of supported catalyst

To prepare the Ti/SAN/MMT, 10 mL of MAO (1M) was added to a 40-mL (10%) SAN/MMT toluene suspension in a nitrogen atmosphere at 70°C. After vigorous stirring for 2 h, the toluene was filtrated, and the precipitate was washed with toluene 5 times. The obtained solid was treated with 20 mL (1×10^{-6} M) of a $\text{Cp}^*\text{Ti}(\text{OCH}_3)_3$ /toluene solution at 70°C for 2 h. Then the toluene was filtrated, and the precipitate was washed with toluene 5 times before being vacuum dried. According to an ICP analysis of the composition of the catalyst, its Ti content was 0.84 mg/g.

The Ti/MMT- and Ti/MAO/MMT-supported catalysts were prepared in a similar way.

Polymerization

The polymerization runs were carried out in 100-mL glass flasks equipped with magnetic stirrers. After being alternately heated and evacuated for about 1 h, toluene, TIBA, unsupported or supported catalyst, MAO, and styrene were introduced into the reactor successively. The polymerization was controlled at 60°C for 4 h, and then terminated with acidified ethanol. The polymerization products were washed with ethanol several times and then dried in vacuum at 60°C for 48 h.

Characterization

The titanium content of the supported catalysts was determined from inductively coupled plasma atomic emission spectroscopy with a Plasma-Dec(I) of America Leeman Lab. The nitrogen content of the SAN/MMT composites was measured by elemental analysis. The M_w and MWD of the polymers were

measured by GPC using a Water 410 GPC, standard polystyrenes as a reference, and 1,2,4-trichlorobenzene as eluent at 140°C. IR spectra of SAN/MMT were recorded on a Bio-Rad FTS 135 spectrophotometer. The T_m of the syndiotactic polystyrene was measured with a Perkin-Elmer DSC-7 instrument at a heating rate of 10°C/min. The X-ray photoelectron spectroscopy (XPS) was measured on a NP-1 X-ray photoelectron spectrometer.

RESULTS AND DISCUSSION

Preparation and characterization of Ti/SAN/MMT-supported catalyst

The key factor in supporting the catalysts on carriers is that the catalyst species can be anchored onto the carriers efficiently without sacrificing the high catalytic activity of the catalyst. To avoid the hydrophilic surface of MMT, which may poison the catalyst, we designed and introduced a medium SAN between the MMT and $\text{Cp}^*\text{Ti}(\text{OCH}_3)_3$. It is well known that MMT has a high degree of water swelling.¹⁴ This phenomenon could possibly be an effective method for the preparation of polymer/MMT composites if an aqueous system were involved. Lee¹⁷ successfully synthesized PS/MMT composites by an emulsion system on the basis of this phenomenon. Accordingly, we synthesized SAN/MMT composites by emulsion polymerization where SAN served as insulator by which the catalytic species could be anchored on the MMT surface.

XPS and IR spectra were used to investigate the process of preparing Ti/SAN/MMT-supported catalysts. Figure 1 presents the IR spectra of MMT and SAN/MMT after extraction. From the contrast of two curves (Fig. 1), it can be seen that SAN/MMT nearly maintained all the characteristic absorption

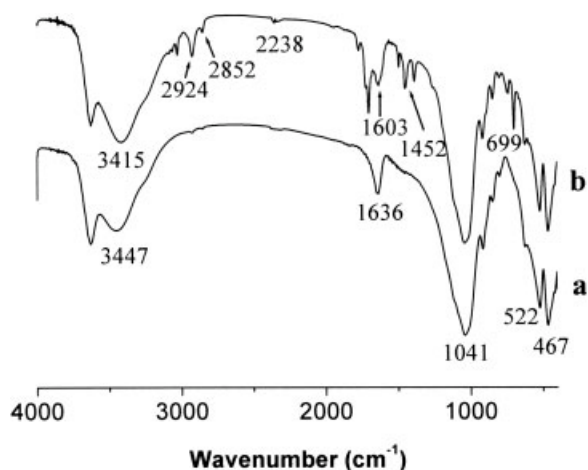


Figure 1 IR spectra of (a) MMT and (b) extracted SAN/MMT.

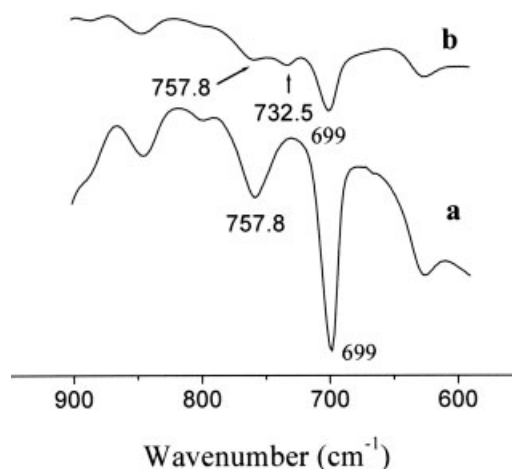


Figure 2 IR spectra of (a) SAN/MMT and (b) MAO-modified SAN/MMT.

bands of MMT: 3447 and 1636 cm^{-1} are characteristic of the stretching and bending vibrations, respectively, of the interlayer water; 1041 cm^{-1} was assigned to Si—O—Si asymmetric stretching vibration; and 522 and 467 cm^{-1} may have resulted from Al—O and Si—O bending vibration. Additionally, there were newborn bands corresponding to SAN: 2238 cm^{-1} could be assigned to the bending vibration of —CN; 2924 cm^{-1} and 2852 cm^{-1} resulted from the —CH₂ asymmetric and symmetric stretching vibrations of polystyrene; and 1603, 1452, and 699 cm^{-1} resulted from the vibration of benzene rings. The IR spectra proved the formation of SAN/MMT composites. Moreover, they confirmed the strong interaction between SAN and MMT because SAN remained even after extraction. According to an elemental analysis, the SAN content in SAN/MMT after extraction was 3.2 wt %.

Figure 2 shows the IR spectra of SAN/MMT and SAN/MMT treated with MAO. Compared with SAN/MMT, the MAO treated SAN/MMT showed a new Al—N absorption band at about 732.5 cm^{-1} ,¹⁸ resulting from the reaction of MAO with MMT. The appearance of the Al—N absorption band suggested that it was SAN not MMT that took part in the reaction with MAO. The SAN indeed served as an insulator.

XPS provided further evidence of SAN as the insulator. Figure 3 shows the binding energy of N_{1s} of SAN/MMT, MAO-modified SAN/MMT, and Ti/SAN/MMT catalyst. The binding energy of N_{1s} of MAO-modified SAN/MMT was 0.3 eV lower than that of SAN/MMT, whereas the binding energy of N_{1s} of Ti/SAN/MMT catalyst was 0.6 eV larger than that of MAO-modified SAN/MMT. Figure 4 shows the binding energy of Al_{2p} of MAO-modified SAN/MMT and Ti/SAN/MMT catalyst. Compared with MAO-modified SAN/MMT, the binding energy of

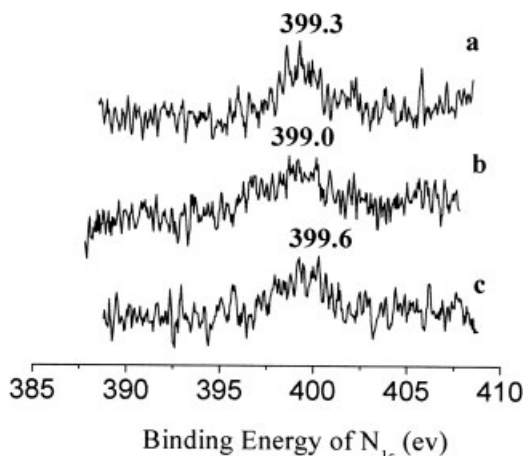


Figure 3 Binding energy of N_{1s} of (a) SAN/MMT, (b) MAO-modified SAN/MMT, and (c) Ti/SAN/MMT-supported catalyst.

Al_{2p} in Ti/SAN/MMT catalyst showed a 0.1 eV increase. The variation in binding energy of N_{1s} and Al_{2p} confirmed that the N in SAN and Al in MAO were the coordination groups of the catalyst. Accordingly, the structure of the supported catalyst could be postulated as in Figure 5.

Polymerization results

Aiming at exploring the effects of chemical properties of MMT surface on the syndiospecific polymerization behavior of styrene, MMT was introduced into polymerization systems in different ways and thus constituted two different catalytic systems: (1) Ti + MAO/MMT *in situ* polymerization systems, with MAO-activated MMT dispersed in polymerization solvent directly followed by polymerization *in situ*; and (2) supported catalyst systems, with Ti/MMT, in which the homogeneous $Cp^*Ti(OCH_3)_3$ was supported on MMT, Ti/MAO/MMT, in which $Cp^*Ti(OCH_3)_3$ was supported on MAO-activated MMT, and Ti/SAN/MMT, in which $Cp^*Ti(OCH_3)_3$ was supported on MAO-activated SAN/MMT. The results of the styrene polymerization over the different catalyst systems are summarized in Table I. TIBA was used as an additional coactivator, as it has been reported that trialkylaluminum compounds enhance the activity of supported catalysts because of the scavenging effect of these Lewis acids.^{16,19} Polymerization results confirmed this view. When MAO and TIBA were used as cocatalysts, homogeneous catalyst systems, supported catalyst systems, as well as *in situ* polymerization system showed higher activity than those catalysts systems whose cocatalyst contained MAO alone.

From Table I, a very interesting phenomenon was noted. When the MAO-modified MMT was dis-

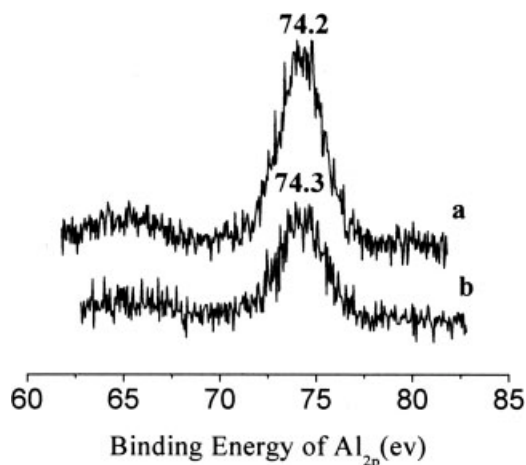


Figure 4 Binding energy of Al_{2p} of (a) MAO-modified SAN/MMT and (b) Ti/SAN/MMT-supported catalyst.

persed in the polymerization solvent directly, the Ti + MAO/MMT catalytic system exhibited very high polymerization activity, even much higher than that of the homogeneous $Cp^*Ti(OCH_3)_3$ catalyst, which gave only a small portion of the syndiotactic polystyrene. These results disagreed with those of Lin, which showed that the addition of MMT did not influence polymerization behavior.¹⁶ Moreover, the T_m of the boiling butanone-insoluble part was 258.8°C, which is far lower than the standard 270°C, suggesting this part was not 100% sPS, but a blend of isotactic polystyrene (iPS) and sPS. These results indicated that the complex chemical properties of the MMT surface facilitated the formation of different active species, which, on the one hand, somewhat enhanced the activity and, on the other hand, facilitated the production of iPS and atactic polystyrene (aPS). It was also affirmed that to produce a polymer with high syndiotacticity, it was essential to introduce a medium between MMT and $Cp^*Ti(OCH_3)_3$.

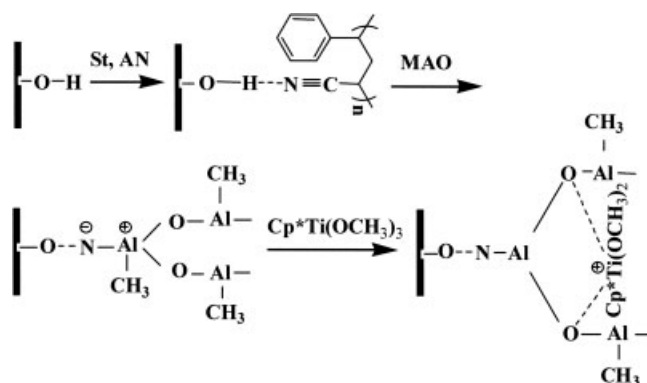


Figure 5 Preparation scheme of Ti/SAN/MMT-supported catalyst.

TABLE I
Syndiotactic Polymerization of Styrene with Different Catalytic Systems^a

Catalyst	[TIBA]/[MAO] ^b	Activity (kg PS mol ⁻¹ Ti h ⁻¹)	Butanone insoluble (%)	T _m (°C) ^c	M _n × 10 ⁻³ (g/mol) ^d	M _w /M _n ^d
Homogeneous	500 : 100	980	96	268.3	150	2.2
	300 : 100	526	—	—	—	—
	100 : 100	179	—	—	—	—
	0 : 600	735	93	268	—	—
Ti/MMT	500 : 100	trace	—	—	—	—
Ti/MAO/MMT	500 : 100	163	—	—	—	—
Ti + MAO/MMT	500 : 100	1265	65.6	258.8	—	—
	0 : 600	910	—	—	—	—
Ti/SAN/MMT	500 : 100	757	78.7	271.7	102	2.7
	300 : 100	512	—	—	180	2.2
	100 : 100	303	—	—	—	—
	0 : 600	606	—	—	—	—

^a Polymerization was carried out in toluene at 60°C for 4 h, [Ti] = 2.5 × 10⁻⁴ mol/L; [st] = 4.3 mol/L.

^b [TIBA]/[MAO] = [Al]_{TIBA} : [Ti]/[Al]_{MAO} : [Ti].

^c Melting point of the butanone-insoluble polymers was measured by DSC.

^d M_n and M_w/M_n of the butanone-insoluble polymers were measured by GPC in 1,2,4-trichlorobenzene at 140°C.

For the supported systems, when the active species were supported neither on MMT directly nor on MMT modified by MAO, the catalyst showed very low polymerization activity, whereas when they were supported on SAN/MMT, the catalyst showed catalytic behavior similar to that of the SiO₂-supported catalyst, with slightly lower or comparable activity and stereospecificity in comparison with the homogeneous catalysts.² It turns out that SAN indeed is an essential component in promoting catalytic activity. The insulator SAN prevented the formation of the inactive/little active species Si—O—Ti resulting from the reaction of —OH on the MMT layer surface with Cp^{*}Ti (OCH₃)₃. Furthermore, the activity of the supported catalysts was still quite high, even at much lower Al/Ti ratios, indicating stabilization of the active sites by the carrier.

Similar to the other supported catalytic system,³ the catalysts immobilized on SAN/MMT gave not only butanone-insoluble polymers but also butanone-soluble polymers. DSC analyses showed the boiling butanone-insoluble part was approximately 100% sPS. The polymers obtained from the supported catalyst had narrow molecular weight distributions with polydispersity below 3.

CONCLUSIONS

MMT was introduced into styrene polymerization systems, and the influence of MMT on polymerization behavior was investigated. SAN, a medium between MMT and Cp^{*}Ti (OCH₃)₃, is an essential component of promoting catalytic activity and syndiotacticity. Both the MMT-supported and MAO-modified MMT-supported Cp^{*}Ti (OCH₃)₃ showed very low

polymerization activity, whereas relative high stereospecificity and activity were obtained with Cp^{*}Ti (OCH₃)₃ supported on SAN/MMT. The main explanation for this is that SAN served as an insulator that prevented the formation of the inactive/little active species Si—O—Ti and other atactic active species.

References

- Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* 1986, 19, 2464.
- Pasquet, V.; Spitz, R. *Macromol Chem Phys* 2001, 202, 2346.
- Soga, K.; Nakatani, H. *Macromolecules* 1990, 23, 957.
- Yim, J. H.; Chu, K. J.; Choi, K. W.; Ihm, S. K. *Eur Polym J* 1996, 32, 1381.
- Xu, J.; Zhao, J.; Fan, Z.; Feng, L. *Macromol Rapid Commun* 1997, 18, 875.
- Pasquet, V.; Spitz, R. *Macromol Chem Phys* 1999, 200, 1453.
- Kaminsky, W.; Arrowsmith, D.; Strubel, C. *J Polym Sci, Part A: Polym Chem* 1999, 37, 2959.
- Soga, K.; Koide, R.; Uozumi, T. *Macromol Rapid Commun* 1993, 14, 511.
- Soga, K.; Monoi, T. *Macromolecules* 1990, 23, 1558.
- Dall'Occo, T.; Sartori, F.; Vecellio, G.; Zucchini, U.; Maldotti, A. *Macromol Chem* 1993, 194, 151.
- Xu, J. T.; OuYang, J. Y.; Fan, Z. Q.; Chen, D. Q.; Feng, L. X. *J Polym Sci, Part A: Polym Chem* 2000, 38, 127.
- Xu, J. T.; OuYang, J. Y.; Fan, Z. Q.; Chen, D. Q.; Feng, L. X. *J Polym Sci, Part A: Polym Chem* 2000, 38, 666.
- Pasquet, V.; Spitz, R. *Macromol Chem Phys* 1999, 200, 1453.
- Solin, S. A. *Annu Rev Mater Sci* 1997, 27, 89.
- Liu, C. B.; Tang, T.; Zhao, Z. F.; Huang, B. T. *J Polym Sci, Part A: Polym Chem* 2002, 40, 1892.
- Shen, Z.G.; Zhu, F. M.; Liu, D.; Zeng, X. G.; Lin, S. A. *J Appl Polym Sci* 2005, 95, 1412.
- Noh, M. W.; Lee, D. C. *Polym Bull* 1999, 42, 619.
- Meng, F. H.; Yu, G. Q.; Huang, B. T. *J Polym Sci, Part A: Polym Chem* 1999, 37, 37.
- Kaminaka, M.; Soga, K. *Makromol Chem Rapid Commun* 1991, 12, 367.